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16TH ANNUAL ARMY ENVIRONMENTAL R&D SYMPOSIUM

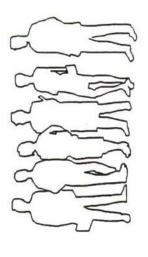
MG JOHN F. SOBKE

23 JUNE 1992



ENVIRONMENTAL CONCERNS





MANDATED BY:

- REGULATORY REQUIREMENTS

CERCLA

SARA

RCRA

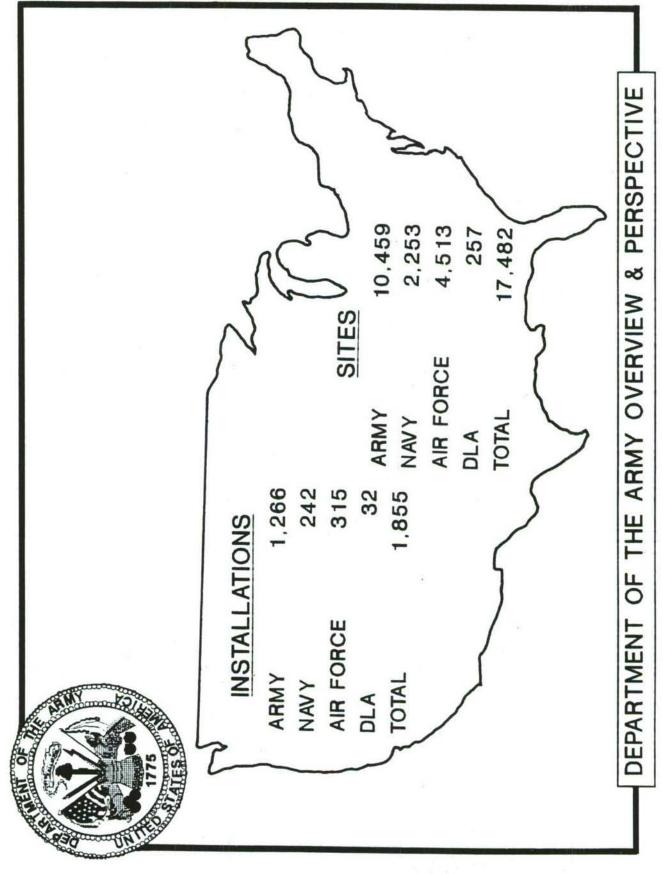
CAA

STRINGENT HEALTH STANDARDS

- INCREASING REMEDIATION AND COMPLIANCE COSTS

- LIMITED RESOURCES





MILITARY UNIQUE COMPOUNDS

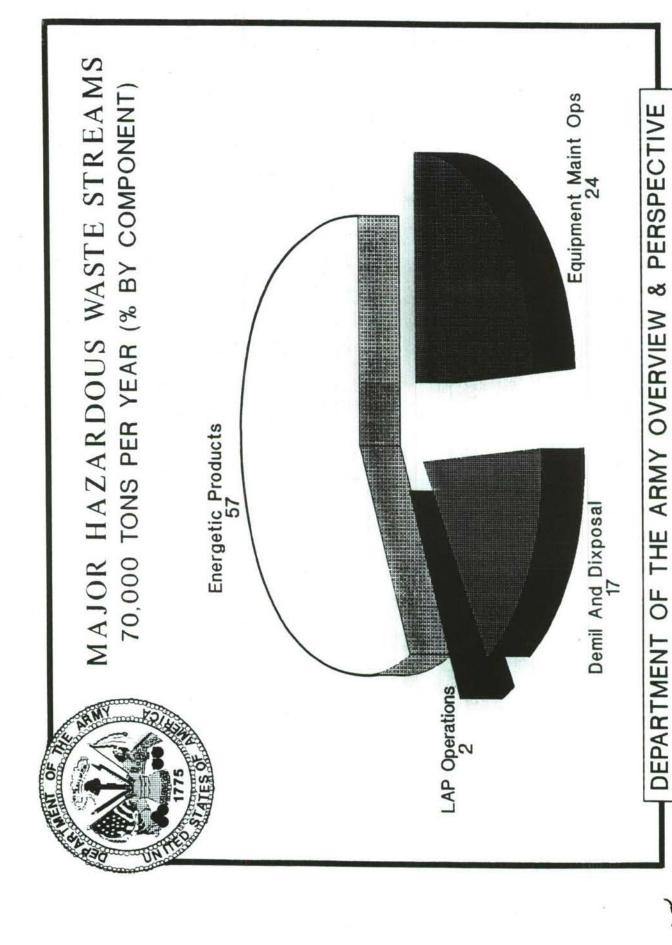


EXPLOSIVES

PROPELLANTS

CHEMICAL AGENTS





PROGRAM DRIVERS

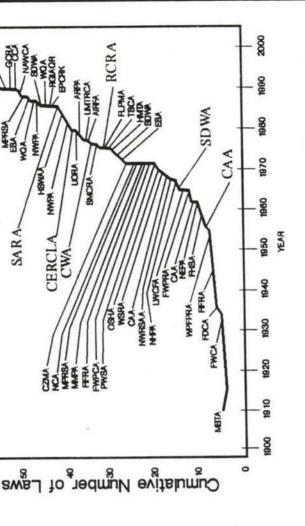


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Regulatory mandate from EPA and states



Increasingly stringent health standards

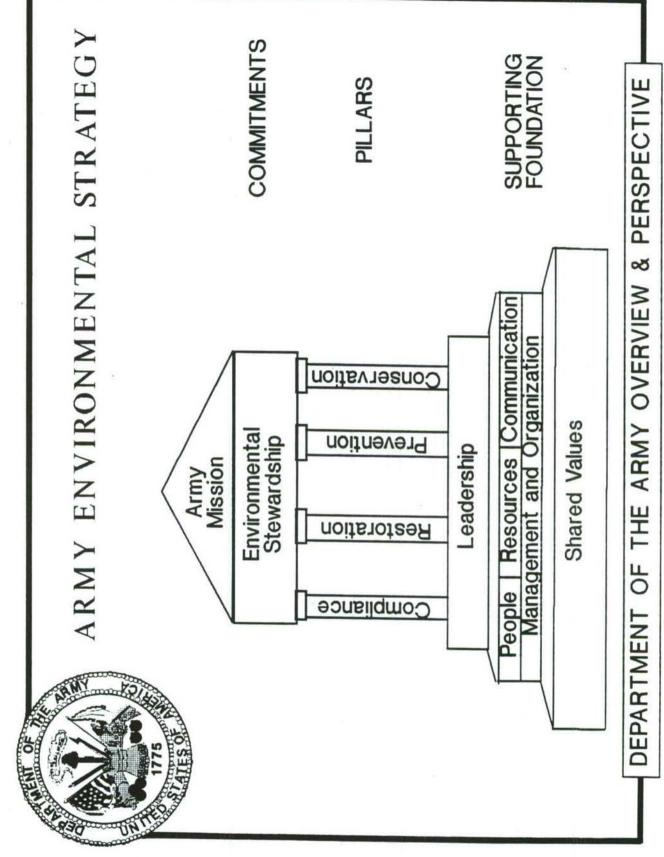


MMA

SARA.

- Demand for analytical methodology to achieve detection and monitoring in ppb-ppt concentrations
- Emphasis on prevention to reduce future cleanup cost
- Increasing costs of environmental compliance

OF THE ARMY OVERVIEW & PERSPECTIVE DEPARTMENT





PROGRAM MAGNITUDE



- FUNDING

- PERSONNEL STAFFING

- ACTIVITY AND REMEDIATION CURRENTLY IMPLEMENTED



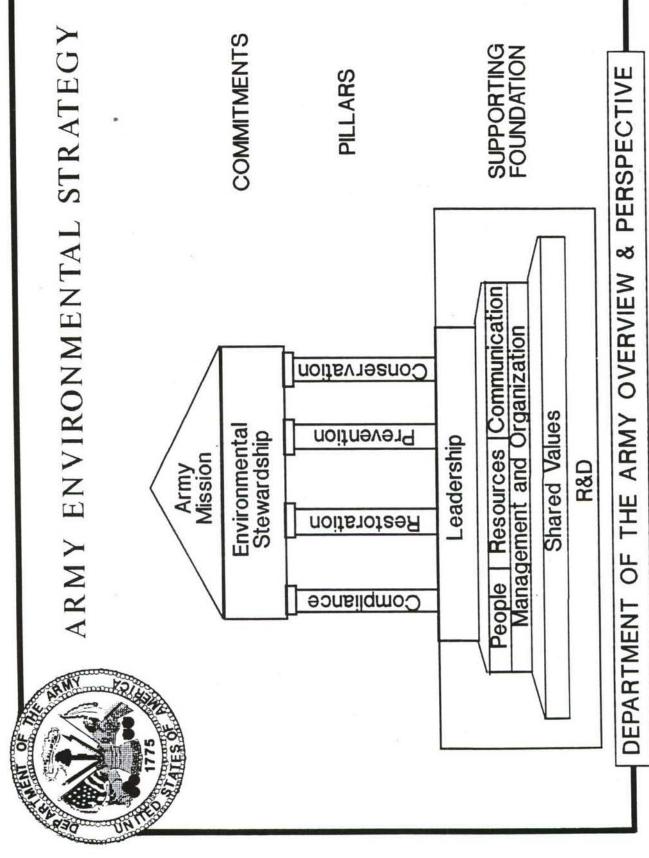
PROGRAM DIRECTION



- GOALS

- INITIATIVES

- SUCCESS STORIES



USER IMPORTANCE

- NEEDS DRIVE THE PROGRAM
- SOUND PROGRAM REQUIRES USER INVOLVEMENT
- TECHNOLOGY TRANSFER



TECHNOLOGY TRANSFER

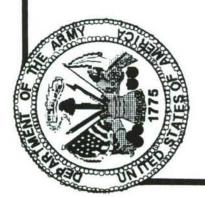


FIELD

COST ANALYSIS **PROCUREMENT**

TECHNICAL TRAINING FEEDBACK

YOUR CHALLENGE



- INSTILL TEAMWORK

- MEET USER NEEDS

CONTINUE STRONG R&D SUPPORT FOR THE ARMY MISSION

THE U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY'S R&D PROGRAMS IN ANALYTICAL CHEMISTRY AND INSTRUMENTS

WARTIN H. STUTZ, GEORGE E. RUBITAILLE U.S. Army Toxic and Hazardous Materials Agency

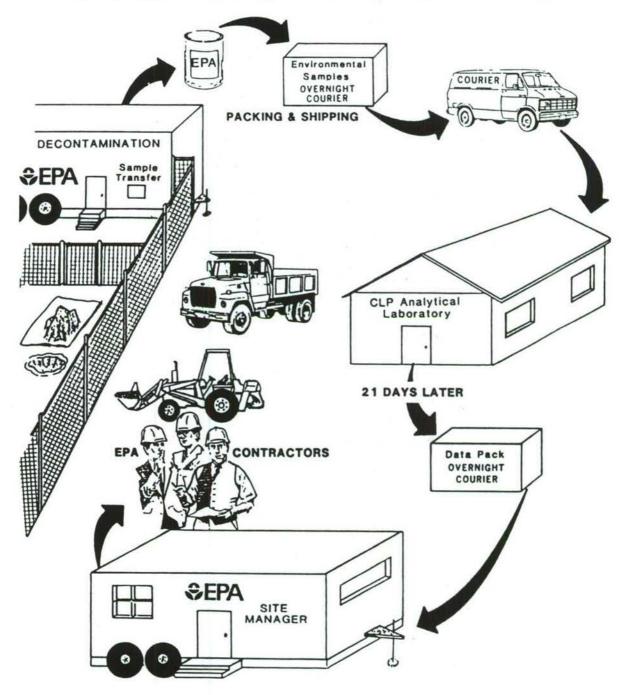
The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is responsible for identifying and cleaning up environmental chemical contamination throughout the Army. A portion of USATHAMA's thrust to accomplish this objective is an ongoing, multifaceted research and development program focusing on the development, testing and validation of new analytical technologies which will contribute to making the investigative and verification of environmental cleanup activities more timely and cost effective, while enhancing quality. Increasing emphasis has been placed on field technologies which can provide field personnel with qualitative and semi-quantitative results during initial field investigations and remedial actions. A secondary objective is the evaluation of materials and procedures and their impact on quality of data, and the identification of improved methods/procedures. This presentation will be an overview of several USATHAMA programs designed to accomplish these objectives.

PROBLEM

NEED TO DEVELOP AND EVALUATE NEW TECHNOLOGIES FOR

- USE IN FIELD
- BE MORE TIMELY
- BE MORE COST EFFECTIVE
- POSITIVE IMPACT ON QUALITY

Traditional Pathway for Sampling and Analysis



Traditional Approach to Site Characterization.

SAMPLE ANALYSIS

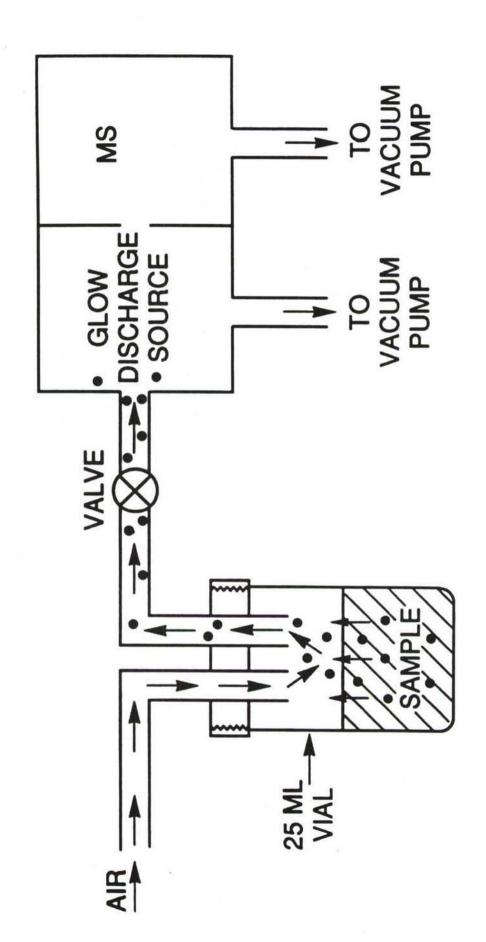
DAY 180	METAL
DAY 47	BNA
DAY 14	VOA
DAY 7	EXTRACT
DAY 2	RECEIVE
DAY 1	CONVENTIONAL TAKE SAMPLE

FIELD

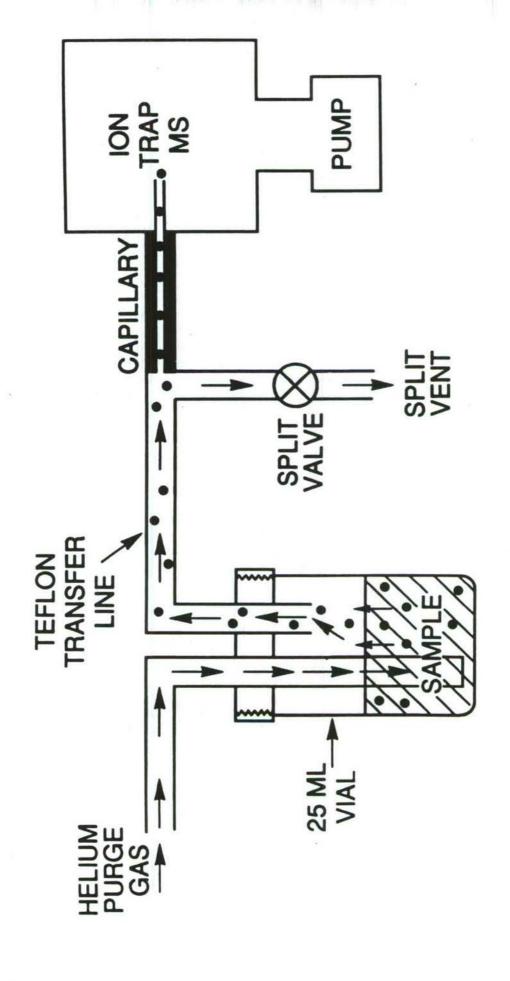
TAKE SAMPLE PERFORM ANALYSIS

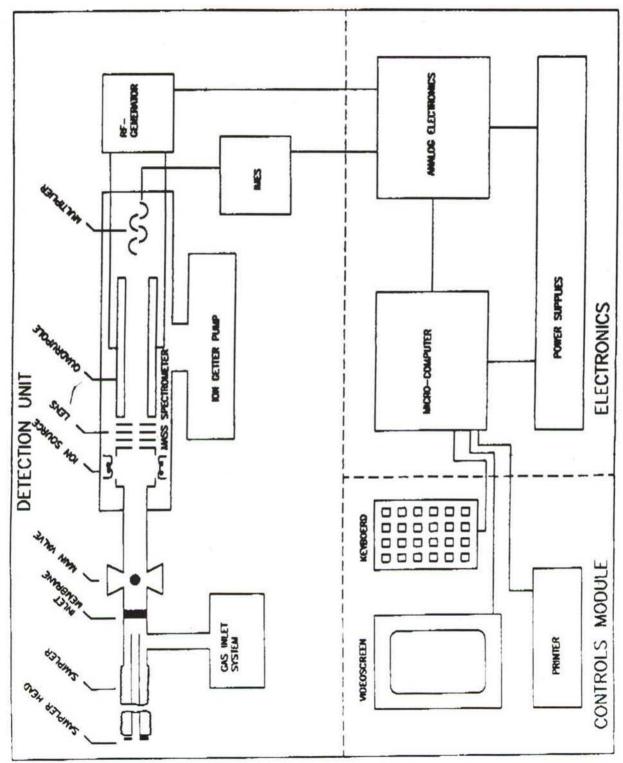
PROGRAMS

- GLOW DISCHARGE MASS SPEC
- ION TRAP MASS SPEC
- PORTABLE GC/MS
- FIELD FTIR
- SOIL GAS SAMPLER



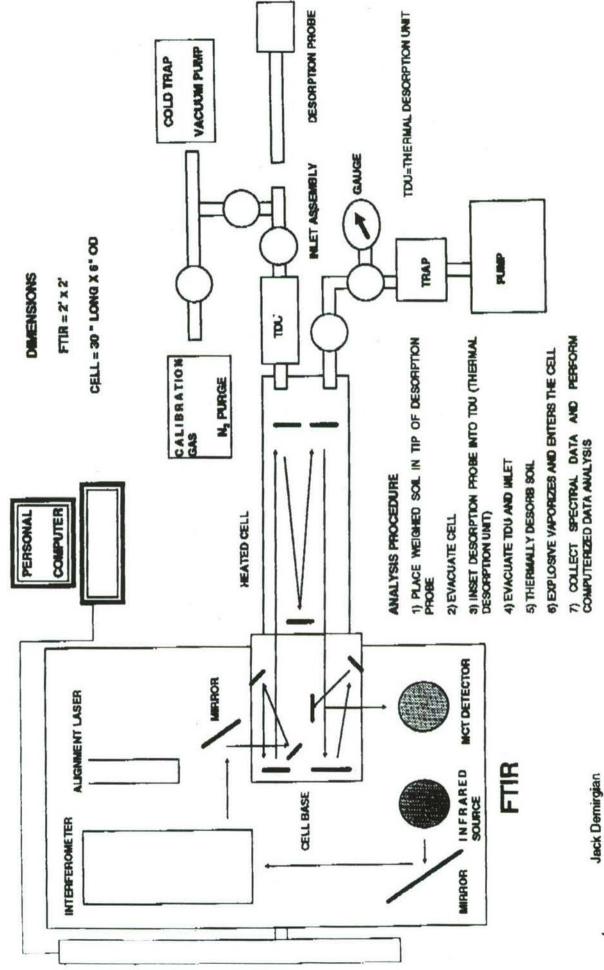
Glow Discharge Sample Inlet for Headspace Analysis





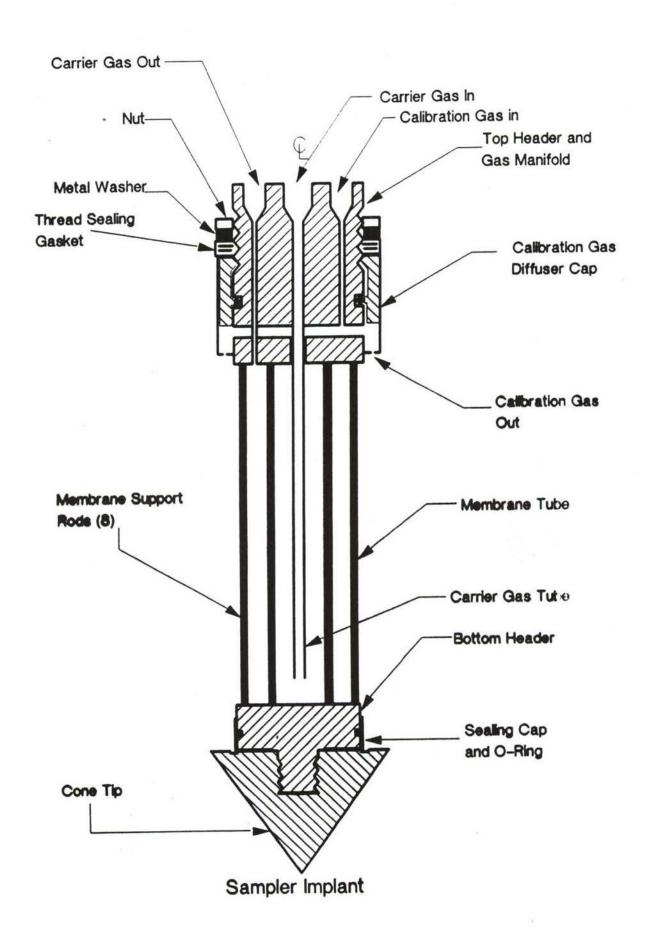
Major Components of the Fieldable GC-MS

DETECTION OF EXPLOSIVES IN SOILS USING FTIR

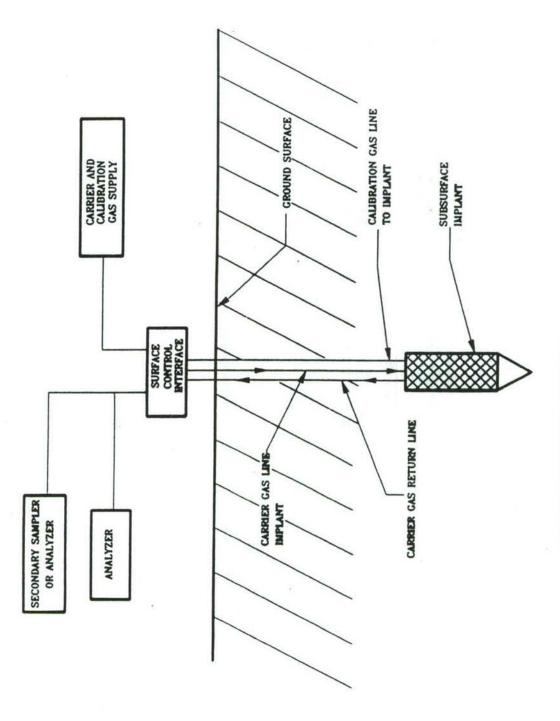


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Argonne National Laboratory





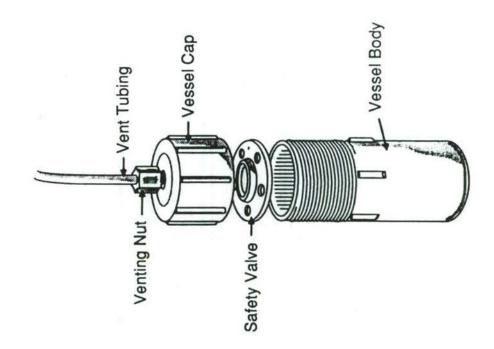


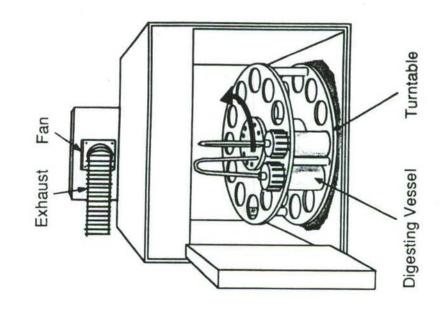
TEPRATROG SOL GAS SAMPLER SYSTEM

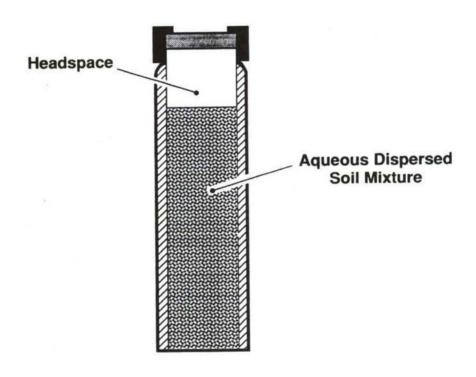
PROGRAMS (CONTINUED)

- FIELD SAMPLE PREPARATION
- FIELD/LAB VOA COMPARISON
- MATERIAL COMPATIBILITY
- DRAEGER TUBE





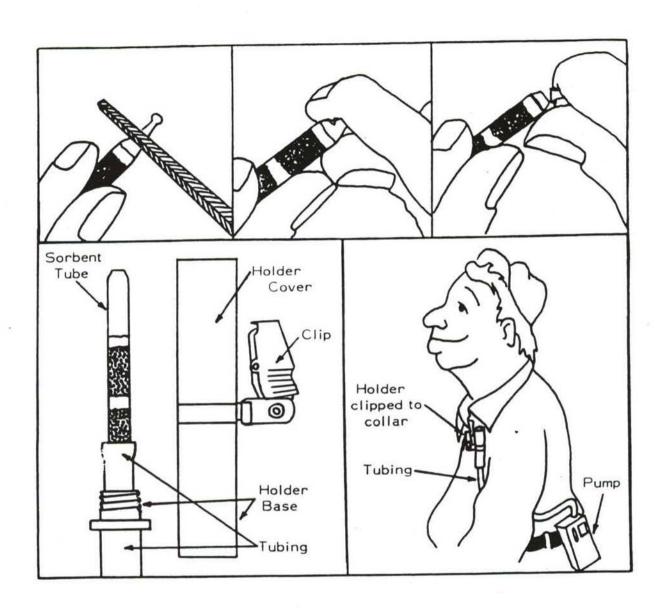




Exposure Vessel

Low-Dissolved-Oxygen Well Water

WELL CASING



PROGRAMS (CONTINUED)

- CHEM AGENT METHODS
- CHEM AGENT BY-PRODUCT
 METHODS

BENEFITS

- COST SAVINGS
- TIME SAVINGS
- DIRECT DETERMINATION
 IN THE FIELD

DEVELOPMENT OF FIELD SCREENING METHODS FOR TNT, 2,4-DNT AND RDX IN SOIL

Thomas F. Jenkins and Marianne E. Walsh U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire

SUMMARY

Simple field-screening methods are presented for detecting 2,4,6-TNT, 2,4-DNT and RDX in soil. A 20g portion of undried soil is extracted by manually shaking with 100 mL of acetone for 3 minutes. After the soil settles, the supernatant is filtered and divided into three aliquots. Two aliquots are reacted with potassium hydroxide and sodium sulfite to form the red-colored Janowsky complex when 2,4,6-TNT is present or the blue-purple complex when 2,4-DNT is present. The third aliquot of the extract is passed through a strong anion exchange resin to remove nitrate and nitrite. Then the extract is acidified and RDX is reduced with zinc to nitrous acid, which is reacted with a Greiss reagent (Hach NitriVer 3 powder pillow) to produce a highly colored azo dye. Concentrations of TNT, 2,4-DNT and RDX are estimated from their absorbances at 540, 570 and 507 nm, respectively. Detection limits are about 1 μg/g for 2,4,6-TNT and RDX and about 2 μg/g for 2,4-DNT. Concentration estimates from field analyses correlate well with laboratory analyses.

INTRODUCTION

Over the past few years, it has become increasingly apparent that the practice of conducting site assessments at hazardous waste sites using off-site contractor laboratories for all analytical chemistry is wasteful in both time and financial resources. The USEPA and USDOE have estimated that between 80 and 90% of all samples collected and analyzed from potential toxic and hazardous waste sites have below detectionresults (analytical zeros). Because these results are obtained using relatively high-cost laboratory methods, these analytical zeros consume a huge portion of the site assessment budget and limit the number of samples analyzed from contaminated zones. Since soil contamination is generally distributed in a non-homogeneous manner, the overall result of this curtailed sampling is poor delineation of zones of contamination. In addition, turn-around times for obtaining results from laboratory

analyses are often weeks to months. This lag time can significantly impact site assessments, reducing efficiency and driving up costs.

One approach to improving assessments at hazardous waste sites is the use of on-site field screening methods for initial site characterization. The use of field portable gas chromatography for volatile organics and field portable x-ray fluoresence for heavy metals are two examples where this approach has proven useful. The objective of the work presented here was to develop field screening methods for some of the Army's most serious environmental pollutants, explosives and propellants.

BACKGROUND

In 1891, Janowski observed that polynitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT) reacted with alkali to form colored reaction products (Janowsky 1891). An enormous amount of research has since been conducted to understand this reaction. The reaction products that result are dependent on a number of factors including solvent system, base used, concentrations of reactants, etc. (Terrier 1982). A simplified version of the reaction of TNT with potassium hydroxide in acetone is shown in Figure 1.

Similarly, the reduction of nitramines such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) with zinc in an acidic medium to form nitrous acid has been known since the 19th Century. This reaction, followed by the classical Griess reaction to form a colored reaction product, has been used for many years by forensic scientists to detect the presence of RDX in post-blast debris (Yinon and Zitrin 1981). A schematic of this reaction sequence for RDX is shown in Figure 2.

Heller et al. (1982) used the reaction of a strong base with TNT as a basis for a field kit for detection of low levels of TNT in water. Erickson et al. (1984) extended the use of this kit to the detection of TNT in soil. This kit is quite effective at detecting the presence

TNT and 2, 4 - DNT Methods
$$CH_3 - C - CH_3 + OH^- \Longrightarrow CH_2 - C - CH_3 + OH^{\bigcirc}$$

$$R \longrightarrow CH_3 + CH_2 - C - CH_3 \longrightarrow CH_3 + CH_2 - C - CH_3 \longrightarrow CH_2 - C - CH_3$$

$$R \longrightarrow CH_3 + CH_2 - C - CH_3 \longrightarrow CH_2 - C - CH_3$$

$$R = NO_2 \text{ for } 2,4,6 - TNT$$

$$R = H \text{ for } 2,4 - DNT$$

Figure 1. Reactions used for colorimetric determination of 2,4,6-TNT and 2,4-DNT.

RDX Method

$$NO_2$$
 NO_2
 NO_2

Figure 2. Reactions used for colorimetric determination of RDX.

of TNT in soil extracts, but estimates of concentration are somewhat subjective (Jenkins and Schumacher 1990). The authors are not aware of other field methods for estimating concentrations of 2,4-DNT or RDX in soil at hazardous waste sites.

DESCRIPTION OF METHOD

For these soil methods about 20 g of wet soil is shaken with 100 mL of acetone to extract the munitions residues, and the extract is filtered using a disposable syringe filter. The methods then depend on the production of colored reaction products (Fig. 3) when three aliquots of these extracts are subjected to two simple reaction sequences. For TNT and 2,4-DNT, portions of the extract are reacted with a strong base and sodium sulfite (Fig. 1). The main difference between the two procedures is the contact time with the reactants before filtration; 3 min for TNT and 30 min for 2,4-DNT. For extracts containing only TNT, a reddish-colored Janowsky complex is produced. For those containing only 2,4-DNT (or 2,4- and 2,6-DNT), a bluish-purple complex is produced.

If 2,4-DNT is present as a minor component and TNT is present at much higher concentration, DNT will not be detectable using this procedure. The DNT procedure is, however, capable of detecting the presence of

DNT in soils contaminated with several types of single-based propellants in which 2,4-DNT is a major component. Several other polynitroaromatics also produce colored complexes and hence are potential interferences (Bost and Nicholson 1935). For RDX another portion of the extract is passed through a disposable anion exchange cartridge to remove any nitrate or nitrite. Then the extract is acidified and reacted with powdered zinc. This converts RDX to nitrous acid, which is detected by adding a Hach NitriVer 3 powder pillow (Fig. 3) and distilled water. The development of a pink color is indicative of the presence of RDX or one of several other military explosives that are potential interferences (HMX, nitroglycerine, PETN or nitrocellulose).

The intensities of the colors produced by these reactions can be measured with a battery-operated spectrophotometer. The absorbances at 540 nm for TNT and 507 nm for RDX are linearly related to concentration. Daily calibration is obtained using a single standard at 2 mg/L. Detection limits are about 1 μ g/g for both TNT (Jenkins, 1990) and RDX (Walsh and Jenkins, 1991a). The linear range extends to 50 μ g/g for TNT and 20 μ g/g for RDX, respectively, for undiluted extracts. The absorbance for the 2,4-DNT complex (570 nm) is dependent on the water content of the extract; thus the

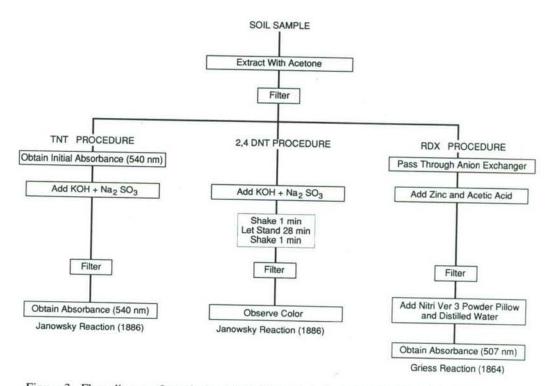


Figure 3. Flow diagram for colorimetric field methods for 2,4,6-TNT, 2,4-DNT and RDX.

method is only semi-quantitative. The detection limit was $2 \mu g/g$ for a standard soil over a moisture content range of 10–50% (wet weight basis) (Walsh and Jenkins, 1991b).

EXPERIMENTAL

Analytical Standards

Analytical standards for TNT and RDX were prepared from Standard Analytical Reference Material (SARM) obtained from the US Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. Test solutions of 2,4-DNT were prepared from reagent grade 2,4-DNT (Eastman Organic Chemicals). Standard materials were dried to constant weight in a vacuum desiccator in the dark, and standard solutions prepared in HPLC grade acetone.

Soils

Soils used for laboratory extraction studies included field-contaminated and uncontaminated soils from a number of present and former military installations in ten different states. Interference tests utilized a humus-rich commercial potting soil obtained locally and uncontaminated soils from a variety of military installations.

Soil Extraction

Munition residues were extracted by manually shaking a 20-g soil subsample for 3 minutes with 100 mL of acetone and filtering the extracts with Millex-SR disposable syringe filters.

Soils were not dried prior to extraction. If a dried soil, or a field soil that appeared dry was used, 3.0 mL of distilled water was added to the soil prior to extraction with acetone.

Generation of the Janowsky Complexes for TNT and 2,4-DNT Tests

For the TNT test, a pellet of potassium hydroxide (KOH) and about 0.2 g of sodium sulfite were added to 25 mL of acetone soil extracts. Samples were manually shaken for 3 minutes, then filtered through a Millex-SR filter unit into a cuvette. Absorbance was read at 540 nm. Unless the extracts contain a large amount of water, the solid reactants do not completely dissolve.

A similar procedure is used for the 2,4-DNT test except that two pellets of KOH and about 0.75 g of sodium sulfite were added, the samples were shaken for one minute, allowed to stand for 28 minutes, then shaken again for 1 minute prior to filtration. Absorbance was read at 570 nm.

Production of an Azo Dye from RDX

Acetone soil extracts were passed through an

Alumina-A strong anion exchange cartridge (Supelco, Inc) at 5 mL/min to remove any nitrate and nitrite which could be present. A 5-mL aliquot was acidified with 0.5-mL glacial acetic acid and reacted with 0.3 g of zinc dust in the barrel of a syringe fitted with a disposable filter unit. This solution was rapidly filtered into a vial containing 20 mL of distilled water. The contents of a Hach NitriVer3 powder pillow were added. The sample was shaken briefly and allowed to stand 10-15 minutes. Absorbance was read at 507 nm.

Spectrophotometers

Spectrophotometers were used to measure absorbance at various wavelengths in the visible region of the spectrum. A Coleman Junior II (Model 6/20) (bandpass 20 nm) was used for laboratory tests and either a Hach DR/2 or DR/2000 (bandpass 12 nm) was used in the field. Path length for the cuvettes was either 19 or 25 mm.

RESULTS AND DISCUSSION

Absorbance Spectra and Molar Absorptivities

The visible absorbance spectra of the colored products produced from standards of TNT, 2,4-DNT and RDX (Fig. 1 and 2) were obtained from 400–700 nm. The absorbance maxima and molar absorptivities are given in Table 1.

The color-forming reactions used for these field screening methods are not specific for TNT, 2,4-DNT and RDX. Other polynitroaromatics such as 1,3-dinitrobenzene (DNB) and 1,3,5-trinitrobenzene (TNB) and polynitrophenols such as picric acid also give colored anions when reacted with strong base. During site cleanup activities, however, the ability to detect these other compounds as well as TNT and 2,4-DNT would be quite useful. Similarly, the same azo dye produced from the RDX test is also produced when other nitramines such as HMX (octahydro-1,3,5,7tetranitro-1,3,5,7-tetrazocine) and tetryl (2,4,6trinitrophenylnitramine) or nitrate esters such as NG (nitroglycerine), PETN (pentaerythritol tetranitrate) and NC (nitrocellulose) are treated under similar conditions. Table 2 is a listing of munition-related compounds detected by these screening procedures.

Effects of Variable Concentrations of Water in Acetone Extracts

In the field, soil extracts will be obtained by manually shaking 20 g of soil with 100 mL of acetone. Since the soil will be moist in most cases, water will be a component of the soil extracts. In addition to a small amount of dilution, the presence of a variable concentration of water may affect the kinetics of these reactions. To investigate this effect, standard solutions of

 $Table \ 1. \ Absorbance \ maxima \ and \ molar \ absorptivities \ for \ colored \ products \ from \ TNT, 2, 4-DNT \ and \ RDX \ field \ screening \ tests.$

Absorbance maxima (λ_{max})	Concentration of standard (mg/L)	Molar absorptivity \times 10 ⁻⁴ (L mole ⁻¹ cm ⁻¹)	Color
462 540	2.1	2.70 1.77	red
570	2.9	1.12	blue then purple
507	4.0	1.67	pink
	maxima (λ _{max}) 462 540 570	Absorbance of standard (mg/L) 462 2.1 540 570 2.9	Absorbance maxima ($λ_{max}$) of standard (mg/L) absorptivity × 10 ⁻⁴ (L mole ⁻¹ cm ⁻¹) 462 540 2.1 2.70 1.77 570 2.9 1.12

TNT, 2,4-DNT and RDX were prepared with water added to simulate the extracts that would be obtained from soils with moisture contents ranging from 0–100% (wet weight basis). For all three analytes, little or no color formed when no water was present (Fig. 4). Over the range of moisture contents (10–75%) that should include the large majority of surface soils from potentially contaminated sites, absorbance varied little for the TNT and RDX solutions. However, absorbance for the 2,4-DNT standard significantly declined for water contents greater than 10%. Based on this variability, determinations for 2,4-DNT will be semi-quantitative while the corresponding procedures for TNT and RDX may be used quantitatively.

Reagent Contact Time

Experiments were conducted to determine if re-

agent contact time had an effect on measured absorbance. Contact time with KOH and $\mathrm{Na_2SO_3}$ was varied from 1 to 18 minutes for TNT and 1.5 to 60 minutes for 2,4-DNT, after which solutions were filtered and absorbances measured. All experiments were conducted at laboratory temperatures (22° \pm 2°C).

Maximum absorbance for TNT was obtained after 3 minutes of continuous shaking (Jenkins 1990). Exposure to the reagents for periods longer than 8 minutes resulted in reduced absorbance at 540 nm. Thus a 3-minute reaction time was selected.

For 2,4-DNT solutions, the time at which maximum absorbance was obtained depended on the water content of the solutions. In general, the absorbance obtained after 30 minutes of intermittent shaking was at least 90% of the maximum (Walsh and Jenkins 1991b). An additional experiment was performed to compare

Table 2. Colors and λ_{max} obtained for acetone solutions of munition related compounds treated with (a) KOH and sodium sulfite or (b) zinc and acetic acid followed by Greiss reagent_a

	. KOH and	KOH and Na ₂ SO ₃		d, Greiss reagent
Compound	Color observed	λ _{max} (400–600 nm)	Color observed	λ _{max} (400–600 nm)
1,3-dinitrobenzene	Purple	570	none	
2,4-dinitrotoluene	Blue	570	none	
2,6-dinitrotoluene	Pinkish-purple	550	none	
1,3,5-trinitrobenzene	Red	460,560		
Tetryl	Orange	460,550	none	507
2-amino-DNT	Pale yellow	400	pink	507
4-amino-DNT	None	_	none	
Nitroglycerine	None		none	12.000
PETN	None	_	pink	507
RDX	None	_	pink	507
HMX	None		pink	507
Picric Acid	Reddish-orange	120	pink	507
2,4-dinitrophenol	Yellowish-orange	420	none	
TNT		430	none	
****	Red	462-540	none	-

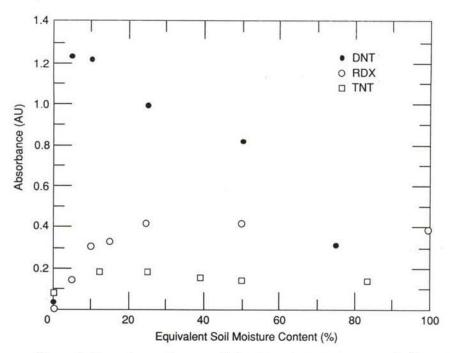


Figure 4. Dependence of measured absorbance on water content of soil extracts.

various shaking protocols. We found that if the solution was shaken initially for 1 minute, allowed to stand for 28 minutes, and then shaken again for 1 minute just prior to filtration, the absorbance obtained was not significantly different from those of protocols that required more shaking (Walsh and Jenkins 1991b). Development of the azo dye from RDX is a two-step procedure. First, the RDX is reacted with zinc dust and acetic acid to produce nitrous acid. The nitrous acid then reacts with a Griess color reagent to produce the azo dye. The amount of time the RDX is allowed to react with the zinc dust and acetic acid was found to be critical (Walsh and Jenkins 1991a). Reaction kinetics are fast when water is present in the acetone extract. Contact times exceeding 30 seconds resulted in less nitrous acid production, presumably because the nitrous acid was further reduced. Once the nitrous acid is produced, the solution must be filtered to remove the zinc dust. Because of the fast kinetics, this filtration is conveniently performed by reducing the RDX in the barrel of a syringe fitted with a disposable filter unit. Once the filtered solution is added to the color-developing solution, full color development takes about 15 minutes.

For all three tests, the colors of the final solutions were stable for at least one hour.

Potential Interferences (other than munitions-related compounds)

Experiments with a variety of blank soils indicated that the color of acetone extracts will vary from colorless to yellow depending on the amount of humic matter present. Background absorbance for the yellow extracts is greatest over the range of 400–500 nm (Jenkins 1990) and for this reason TNT determinations are made at 540 nm rather than at 462 nm, despite the lower molar absorptivity at 540 nm (Table 1). After soil extracts are reacted with KOH and Na₂SO₃ for 3 minutes, the absorbance at 540 nm approximately doubles; thus an initial absorbance measurement must be made on aliquots of acetone extracts subjected to the TNT screening procedure and the DNT procedure as well, if used quantitatively. The initial absorbance is doubled and subtracted from the final absorbance to estimate TNT concentration.

As will be discussed later, heavy metal cations such as copper were found to interfere with 2,4-DNT determinations. These cations could form complexes with either the unreacted DNT (Leggett 1991) or the Janowsky complexes, thereby reducing the concentration of the colored Janowsky complex and hence the detectability of 2,4-DNT.

For the RDX test, background absorbance from humic material is not a problem. Once the acetone extract is acidified and mixed with the color-forming reagent, the humic material precipitates and may be removed by filtration. Experiments with a wide variety of blank soils showed that background was negligible in all cases (Walsh and Jenkins 1991a).

Since the RDX test measures nitrous acid concentration, soil samples containing nitrite or nitrate would

Table 3. Comparison of extraction efficiency of field procedure and standard laboratory procedure.

			Concentrat	tion (μg/g)	_
Sample origin		Analyte	Field procedure*	Lab procedure**	Recovery (% by field proc.†
Nebraska Ordnance Plant	Α	TNT	0.065	0.071	91.5
	В	TNT	340	349	97.4
	C	TNT	63.5	67.9	93.5
	D	TNT	0.39	0.32	122
Hawthorne AAP (Nev).	A	TNT	4.53	4.75	95.4
	В	TNT	5.79	5.65	102
	C	TNT	0.79	0.90	87.8
Weldon Springs (Mo.)	A	TNT	0.96	1.26	76.2
	В	TNT	163	176	92.6
	C	TNT	0.075	0.077	97.4
Vigo Chem. Plant (Ind)		TNT	11.7	13.4	87.3
Hastings East Ind Park (Neb)		TNT	67.6	68.8	98.3
Sangamon Ordnance Pt. (II.)		TNT	21.5	23.2	98.2
Raritan Arsenal (NJ)		TNT	71.7	80.6	98.0
Lexington-Bluegrass Depot (Ky)		TNT	5.90	7.11	83.0
Chicksaw Ordnance Works (In)		TNT	0.21	0.16	131
Nebraska Ordnance Plant	Α	RDX	13.6	14.1	98.3
	В	RDX	60.2	65.9	95.5
	C	RDX	1073	1080	99.7
	D	RDX	9001	10,445	92.6
Hawthorne AAP (Nev)	A	RDX	1.97	2.01	99.0
	В	RDX	3.32	2.96	105
Lexington Bluegrass Depot (Ky)		RDX	9.10	9.37	98.5
Camp Shelby (Ms.)	A	2,4-DNT	3.4	4.2	80.9
	В	2,4-DNT	226	563	40.1
	C	2,4-DNT	6.7	7.3	91.8
Eagle River Flats (Ak)	A	2,4-DNT	12.7	13.6	93.4
	В	2,4-DNT	7.4	7.7	96.1

^{* 20} g of soil shaken with acetone for 3 minutes.

give a false positive if the nitrite and nitrate are not removed prior to reaction of RDX with zinc. This is accomplished by passing the extract through a disposable 3-mL strong anion exchanger (Supelco Alumina A). Experiments indicate that over 98% of the nitrate in a 9.8-mg/L test solution was removed using this procedure (Walsh and Jenkins 1991a).

Extraction Efficiency of Field Procedure

For a field method to provide accurate estimates of analyte concentration in the soil, the extraction step must be rapid enough for field use. Previous extraction studies indicated that long extraction times were required when acetonitrile or methanol were used as the

extraction solvent for nitroaromatics and nitramines (Jenkins and Grant 1987).

In order to determine how rapidly acetone will extract TNT, 2,4-DNT and RDX from soil, field-contaminated soil samples from 14 different sites were extracted with acetone using 3 minutes of manual shaking. An aliquot of the extract was removed and the remaining soil/acetone slurries placed in an ultrasonic bath for 18 hours. Both sets of extracts (3 minutes and 18 hours) were analyzed by RP-HPLC as described elsewhere (Jenkins et al. 1989). The results are presented in Table 3. The average recovery after 3 minutes of manual shaking with acetone was 96% for TNT and 98% for RDX of that obtained with the more exhaustive

^{** 20} g of soil extracted with acetone for 18 hours in sonic bath.

[†] Relative to laboratory procedure.

procedure, indicating that acetone is an excellent extraction solvent with respect to its extraction kinetics for these two analytes over a wide concentration range (Jenkins 1990, Walsh and Jenkins 1991a). The average recovery for 2,4-DNT was only 80.5%, with one low recovery (40.1%) for the soil with highest 2,4-DNT concentration (Walsh and Jenkins 1991b). Overall, the extraction efficiencies for all three analytes are sufficient for a field screening method.

Comparison of Analyte Concentration Estimates

The field screening procedures were first tested in the laboratory using previously air-dried field-contaminated soils. Prior to extraction, the soils were wetted to simulate the moisture that would normally be present under field conditions. Estimates of analyte concentrations obtained by the colorimetric field procedure were correlated against those obtained by the standard RP-

HPLC method. The colorimetric results for TNT were correlated with both the TNT estimate by HPLC and the sum of TNT and TNB. The best correlation was found with the sum of TNT plus TNB and resulted in a slope of 1.15 and an R2 of 0.985 (Fig. 5). A paired t-test indicated that the concentration estimates for TNT from the colorimetric method and the sum of TNT and TNB by the HPLC procedure were not different at any level of significance (Jenkins 1990). Thus it appears that the colorimetric results are best represented as the sum of TNT plus TNB. The slope of 1.15 indicates that, in general, the colorimetric procedure gives a slightly greater estimate for TNT than can be accounted for by TNT and TNB (Fig. 5). One interpretation of these results is that other TNT degradation products such as trinitrobenzoic acid, trinitrobenzyl alcohol, and trinitrobenzaldehyde (Walsh 1990), which are not identifiable by RP-HPLC analysis of the extracts, also form

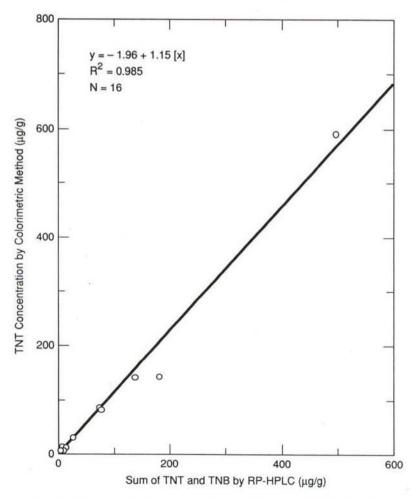


Figure 5. Correlation of concentration estimates for TNT using the field method with the sum of TNT and TNB by RP-HPLC.



Table 4. Comparison of colorimetric and RP-HPLC analysis of soil extracts.

	Colorimetric	RP-HPLC method		
Sample origin	method (µg/g)	2,4-DNT (μg/g)	2,6-DNT (μg/g)	
Camp Shelby (MS)—A	3.3	3.4	0,6	
Camp Shelby (MS)—B	203	226	12.1	
Camp Shelby (MS)—C	5.0	6.7	0.2	
Eagle River Flats (AK)—A	11.4	12.7	0.9	
Eagle River Flats (AK)—B	0.8	7.4	0.5	

colored Janowsky complexes, thereby producing positive interference.

While we do not believe that the 2,4-DNT procedure can be used quantitatively in the field because calibration depends on water content, we tested the method in the lab with air-dried soils wetted such that the moisture content was 10%. This moisture content was chosen since absorbance would be close to maximum, based on the previous experiment on the effect of water content. Only five soils were available that were contaminated primarily with 2,4-DNT. These soils were collected from explosive ordnance disposal sites. Results are given in Table 4. The field procedure severely underestimated the concentration of 2,4-DNT in one sample from Eagle River Flats, Alaska. This particular sample was also contaminated with copper (347 µg/g). As discussed previously, copper is a potential interferant since it may complex with 2,4-DNT or the Janowsky complex. Correlation between estimates for the remaining four samples was excellent (> 0.999); however, the field procedure underestimated 2,4-DNT concentration by 15-25%.

To further explore the potential for false negatives, a series of soils from a number of Army installations that had been previously determined to be free of munition residues were spiked with 2,4-DNT and analyzed by the field screening procedure. In all cases 2,4-DNT was easily detected, but as observed earlier, the measured concentrations were consistently lower than anticipated by up to 30% (Walsh and Jenkins 1991b). The magnitude of interference observed for the Eagle River Flats sediment was not observed in any of these soils.

Eleven field-contaminated soils were used to compare the RDX concentrations estimated by the field method with those obtained by RP-HPLC analysis. The results using the field method were correlated with those obtained by the HPLC method for both RDX alone and the sum of RDX and HMX. The best correla-

tion was obtained with RDX plus HMX and resulted in a slope of 0.9 and an R² of 0.995 (Fig. 6). Paired *t*-tests indicated that the estimates of RDX concentration obtained by the field procedure were not significantly different (0.05 significance level) from those obtained by the HPLC procedure for RDX alone or for the sum of RDX and HMX.

Estimation of Detection Capability

The reporting limits of TNT and RDX concentrations using these field procedures were established using the method of Hubaux and Vos (1970) as adapted by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA, 1990). The calculated certified reporting limits were 0.72 and 1.4 μ g/g for TNT and RDX, respectively.

The reporting limit for 2,4-DNT was $2 \mu g/g$ based on a certification procedure for methods that simply screen for contamination (USATHAMA, 1990). For the certification procedure four soils were spiked at a chosen concentration, in this case $2 \mu g/g$. These soils, along with four soil blanks, were processed according to the method. After color development, four individuals were asked to distinguish the soil spikes from the blanks. Certification was performed three times, each at a different soil moisture content (10, 25, and 50% wet weight basis). In all cases, the soil spikes could be distinguished from blanks with 100% accuracy at $2 \mu g/g$.

Field Testing

Both the TNT and RDX procedures have been field tested and the concentration estimates obtained in the field compared with those obtained on separate subsamples processed by the standard laboratory procedure (acetonitrile extraction followed by RP-HPLC determination, Jenkins et al. 1989). Results are presented in Table 5.

The TNT procedure was initially tested at Umatilla

Army Depot, Oregon. Since TNT concentrations were expected to be very high, a smaller subsample of soil was used and the extracts diluted before reaction with KOH and Na2SO3. This field test was conducted before the importance of reagent contact time was understood. Contact times of 10 minutes were used. Except for one sample, the results of laboratory analysis were higher than those obtained using the field method. This sample had a TNT concentration an order of magnitude higher than any of the other samples and was not included in this correlation. Correlation analysis was conducted comparing the field and laboratory results on the remaining 10 samples. This analysis resulted in an R2 value of 0.865, which was significant at the 99% confidence level. The slope of the best fit relationship was 0.627, indicating the field procedure, on the average, gave results only about 63% as high as the laboratory results.

Two factors may have contributed to the low results for the field method. First, an excessively long reagent contact time prior to filtration was used for the samples. Thus the absorbance would have been reduced relative to its maximum value. Second, the TNT concentrations in the Umatilla soil were much higher than those in the other field-contaminated soils tested, and the percentage extracted in the short extraction time used by the field method could have been reduced compared to the 18-hour extraction with acetonitrile used in the laboratory procedure. Nevertheless, the field results were encouraging for a first test.

The RDX method was field tested in Newport, Indiana, by Dr. Richard Coghlan, Dames and Moore Corp. Correlation between estimates for all 11 samples yields a correlation coefficient of 0.95. However, the slope of the best fit relationship is only 0.36. This low value for the slope is strongly influenced by the last data point, where the estimates of RDX concentration were 4300 and 12,000 µg/g for the field and laboratory procedures, respectively. If the comparison is made using only those soils that had absorbances for the field procedure within the linear range (less than 0.7 absorbance unit) without dilution of the acetone extract, the R² value is 0.94 and the slope is 0.95. We feel this comparison is justified because we wish to distinguish the boundary between uncontaminated and contaminated soil in a field screening test, making accuracy at the lowest concentrations most important.

The TNT and RDX methods were also field tested at Eagle River Flats, Alaska, and Camp Shelby, Mississippi. Forty samples were screened at Eagle River Flats:

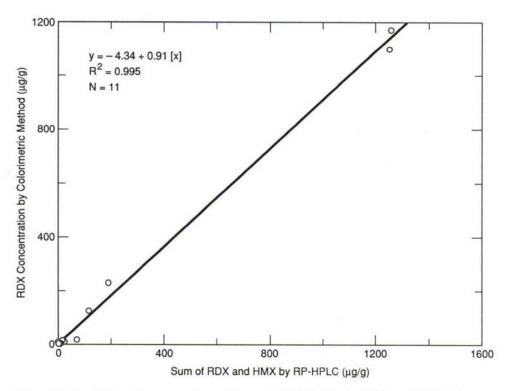


Figure 6. Correlation of concentration estimates for RDX using the field method with the sum of RDX and HMX by RP-HPLC.



Table 5. Comparison of concentration estimates from the field procedure and the standard laboratory procedure. Determinations made on separate subsamples.

Concentration (lg/	(g)
-----------------	-----	-----

		ΓNT	F	RDX
Site	Field† procedure	Lab procedure	Field† procedure	Lab procedure
Umatilla Depot Oregon	1060	2250	NT*	NT
	3560	7430	NT	NT
	704	1180	NT	NT
	3180	4030	NT	NT
	4490	8520	NT	NT
	2530	3990	NT	NT
	84	131	NT	NT
	102000	38600	NT	NT
	6610	7690	NT	NT
	109	183	NT	NT
	716	1300		
Newport, Indiana	NT	NT	< d	0.05
	NT	NT	1.0	1.31
	NT	NT	1.7	3.15
	NT	NT	6.0	15.5
	NT	NT	6.8	8.4
	NT	NT	160	299
	NT	NT	38	38.6
	NT	NT	48	258
	NT	NT	660	1800
	NT	NT	2100	3170
	NT	NT	4300	12,200

^{*} NT = not tested

all gave negative tests. The samples were subsequently analyzed by RP-HPLC and no explosive residues were detected in any sample. Some practical information was gained from this field test. Both KOH and Na₂SO₃ are hygroscopic and should be protected from moisture under humid conditions by keeping reagent bottles tightly closed. Low ambient temperatures caused two problems. First, glacial acetic acid freezes at 16.6°C (62°F). Second, reagent contact times for the TNT procedure had to be extended. The optimum time, which depends on temperature, was determined by observing the color development in a spiked sample.

At Camp Shelby, 22 samples were screened. Three samples gave positive indications for the presence of TNT, but no TNT was observed in these three samples by RP-HPLC. All three contained 2,4-DNT, as

did some of the other samples, one of which was observed to give a purple color in the field TNT test. Nineteen of the soils gave a positive field screening response for the RDX test. RDX was only detected by RP-HPLC in one of these soils. However, the RDX tests will also give a positive response for nitrocellulose (NC). NC is the primary component of single, double and triple base propellants. 2,4-DNT is an additive of single base propellant and its widespread presence at this site probably indicates the NC is present as well at even higher concentrations. In fact, propellant grains were observed scattered about the area. However, the soils were not analyzed for NC, since there is no reliable analytical technique to determine this compound in soil. So the explanation for false positives for the Camp Shelby samples must remain speculation. It should be pointed out that soils from this site were taken from

[†] Not corrected for moisture

Table 6. Comparison of TNT estimates from the colorimetric field screening method and the laboratory RP-HPLC procedure (Dixon, personal communication).

TNT Concentration (µg/g)

Field screening	Laboratory RP-HPLC			
< d	0.13			
102,000	73,000			
4.4	1.8			
29.1	23.7			
52.0	54.2			
8.2	5.5			
5.4	5.5			
21.3	22.6			
25.9	17.5			
	< d 102,000 4.4 29.1 52.0 8.2 5.4 21.3			

areas that served as both an explosive ordnance disposal area and an artillery impact area and could have traces of a wide variety of munition compounds.

Additional field validation of these procedures has been conducted independently by several contractors doing site assessments at Department of Defense installations. Aquatec, Inc., compared results of the field screening method for TNT (Jenkins 1990) with the laboratory RP-HPLC procedure (Jenkins et al. 1989, Chirgwin personal communication). A total of 163 soil samples from Seneca Army Depot were screened, 18 showing a positive field screening results. When 15 of these positives were extracted and analyzed by the laboratory procedure, 9 had measurable levels of TNT, 2 had 2,4-DNT and 2 had trinitrobenzene (TNB). Only 2 samples proved to be false positives.

Chirgwin (personal communication) also extracted and analyzed 56 soils that gave negative results using the TNT field screening method. All proved to be blank using the laboratory method, indicating the procedure does not suffer from large numbers of false negatives.

Wayne Dixon of Dames and Moore Corporation screened a number of soils from Savanna Army Depot for TNT and RDX using these field screening procedures (Dixon personal communication). RDX was not detected in any of these soils and was not detected in 9 samples analyzed by the laboratory procedure. TNT was detected in 8 samples using the field procedure and TNT was detected in all 8 soils using the laboratory

method. TNT concentrations obtained by the two procedures are presented in Table 6.

CONCLUSIONS

Simple field screening methods were developed for detecting 2,4,6-TNT, 2,4-DNT and RDX in soil. The procedure involves the extraction of munition residues from a soil subsample with acetone. Three portions of the extract are then reacted to two sets of reagents that form colors in the presence of nitroaromatics or nitramines. Concentration estimates obtained by this colorimetric procedure compared favorably with those obtained by the standard laboratory procedure. Field tests were conducted and the methods were found to be usable under field conditions. Comparisons of the results from the field screening procedures with the standard RP-HPLC method were excellent.

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This publication reflects the personal views of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or Government of the United States.

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Multiple Uses and Applications of the Bruker Mobile Mass Spectrometer MM-1 for the Detection of Chemical Warfare Agents and other Hazardous Substances

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Introduction

The 1992 Earth Summit held in Rio de Janeiro represents a unified desire for international governments to work together to discuss issues related to environmental hazards and the extensive pollution which has become so eminent throughout the world. We are all to familiar with countless situations of environmentally unsound activities which sometimes result in an irreversible degradation of our environment. In some cases, for reasons of greed and illegal irresponsibility, man has purposely created a negative impact on the environment. Activities such as the dumping of chemicals and sewage into our rivers and oceans, the leaking from underground storage tanks and other buried containers of waste, the emission of chemicals into the atmosphere, and the unfortunate consequences of contamination from accidents such as fires and overturned-ruptured transportation vehicles all add to the negligence and mistreatment of our planet.

Conventional means (environmental laboratories) for monitoring pollution in the environment has allowed the identification, and mapping of chemical contamination yielding information about the pollution. Unfortunately the number of sites which are contaminated, and the extent of pollution, is often much greater than originally believed. The amount of time needed to properly monitor and remediate these sites often takes several Of the large number of samples which are sent to a laboratory for analysis, many are clean of contamination because the sampling crew has little knowledge of where the contamination Additionally, the results from samples are not known for several weeks to a month after sample collection.

Innovative Technology

Promoting successful alternative technologies can improve the efforts associated with site remediation. The Mobile Mass Spectrometer (MM-1) is an example where an alternative technology to conventional practices and procedures has been used to combat many problems associated with the detection and monitoring of organic contamination on site. The MM-1 has been an integral part of the US Army Nuclear, Biological, Chemical Reconnaissance Systems (NBCRS) Program and is the only mil-spec Gas Chromatograph Mass Spectrometer system accepted by the military for the monitoring of chemical warfare agents used during hostile conditions. Likewise,

the desire of national governments to protect their populations from environmental hazards has allowed the resources of the military to be applied to solving similar environmental problems throughout the world. As a result of this technology transfer, the MM-1 has been achieving acceptance for its ability to provide rapid on-site identification of hazardous contamination at Superfund sites as well as other heavily polluted sites worldwide.

Table 1. SITE Monitoring and Measurement Technologies Program Participants¹

Developer	Technology	Waste Media	Applic. Waste
Bruker Instruments, Inc., Billerica, MA	Mobile Environmental Monitor	Water, Air Soil, Sludge, Sediment	VOCs and SVOAs
Analytical and Remedial Tech, Inc., Menlo Park, CA	Automated VOA System	Water, Air	VOCs
Binax Corp., Antox Div., S. Portland, ME	Equate Immunoassay	Water	VOA PAHs
CMS Research Corp., Birmingham, AL	MINICAMS	Air	VOCs
Ensys, Inc., RTP, NC	ELISA	Water	PCPs
Graseby Ionics, Ltd., Watford, Herts, England and PCP, Inc., West Palm Beach, FL	Ion Mobility Spectrometry	Air, Vapor, Soil, Water	VOCs, Chloroform, Ethylbenzene
HNU Systems, Inc., Newton, MA	Portable GC	Air	VOCs, Aromatic, Halocarbons
MDA Scientific, Inc., Norcross, GA	Infrared Spectrometer	Air	Non-specific Organics
Microsensor Systems, Inc., Springfield, IL	Portable GC	Air	VOCs
Microsensor Tech., Inc., Fremont, CA	Portable GC	Air	Non-Specific Organics
Photovac International Inc., Deer Park, NY	Photovac 10S Plus	Air	VOCs, Chlorinated Olefin Comp.
Sentex Sensing Tech. Inc., Ridgefield, NJ	Portable GC	Air, Water, Soil	VOCs
SRI Instruments, Torrance, CA	GC	Air	VOCs
XonTech, Inc, Van Nuys, CA	XonTech Sector Sampler	Air	VOCs

Table 1 lists numerous SITE Monitoring and Measurement Technologies Program participants who have demonstrated innovative technologies for on site monitoring. Unlike the other existing technologies, the MM-1 is the only single detector which allows for the fullest

range of organic analytes to be measured in all matrices of air, soil, and water samples with the capability to detect the fullest range of organics from volatile freon to semi-volatile PAH's and PCB's.

Mobile Mass Spectrometer

The MM-1 has been designed to provide all the essential operating characteristics which make it unique and desirable for a wide variety of uses in the field. It was built specifically to be rugged, provide unambiguous identification, generate real-time results on site, require no preparation of airborne and surface samples prior to analysis, and be simple to operate.

The MM-1 can be mounted on a cart and brought indoors for on site monitoring and/or mounted in a road vehicle to perform outdoor measurements. This compact easy to use system provides the specificity, sensitivity, flexibility and adaptability to yield rapid data output on a real time basis.

Unique hardware features of the MM-1 include a dual filament impact ion source, a hyperbolic one piece quartz electron quadrupole and a 17 stage Cu-Be electron multiplier. A silicon membrane has been incorporated as the interface. An ion getter pump based vacuum system is used to increase the operating lifetime of the high vacuum components while providing for mobility to reduce or eliminate system set-up time. The use of purified ambient air as the carrier gas allows for the elimination of gas cylinders. The MM-1 requires low power and is designed for battery operation and complete mobility without additional external heating or cooling allowing the MM-1 to arrive at the site already set up and ready for analysis. The MM-1 autotunes, autocalibrates, and automatically monitors instrument performance and calibration by incorporating an extensive internal diagnostics routine. Additionally, an auxiliary MS-DOS 80386 GC/MS data system offers full capabilities for storage, retrieval, processing and archival of data files.

MM-1 Sampling accessories

An equally important design goal of the MM-1 is to reduce sample preparation. The membrane inlet system and flexible sample inlet devices are designed to greatly reduce sample preparation and increase system reliability. The following sample inlet devices allow for a variety of sample introduction techniques.

Combination Air/Surface Sampling Probe

Consists of a large heated silicone membrane head followed by a 3.5 Meter capillary GC column encased in an elongated temperature programmable heated tube, ending at the membrane separator inlet to the MS ion source. This configuration allows for the probe head to be easily moved to the area measured. A continuous flow through the column enables the continuous measurement of ambient air, vaporization of solvent extracts, as well as direct contact thermal desorption of a surface which transfers the organic analytes into the MS ion source without any sample preparation.

Gas Chromatograph Oven

A mini Gas Chromatograph oven which is temperature programmable houses a capillary column up to 30 Meters in length. It is equipped with a thermal desorption chamber which allows the introduction of standard sorbent tubes, as well as providing direct injection capabilities of standards and solvent extracts. This oven is advantageous when a complex mixture of analytes need to separated and detected. Filtered ambient air is used as the carrier gas.

Ultra Fast Soil Sampler

The soil sampler is the same 3.5 Meter capillary GC column configuration as the probe (including probe head) but without the flexible tube. The capillary column is encased in an oven equipped with a cooling fan for extremely rapid heating and cooling. The auto-sample injection platform allows for reproducible injections.

Automatic Air Sampler

This computer controlled device can be attached to the GC oven. An internal pump passes air samples through a sorbent tube for enrichment. Analytes are then desorbed from the tube and transferred to the GC column for analysis. Unattended operation of an unlimited number of air, water and soil samples can be automatically performed.

Spray Extractor Water Sampler

The spray extractor is an exciting alternative to the conventional purge and trap technique. In spray and trap, instead of bubbling air through a sparging vessel, the liquid is sprayed through a nebulizer resulting in tiny water droplets being formed. This provides a larger contact surface between the liquid and the air to achieve a highly efficient extraction of volatile organic compounds. The analytes are then concentrated on a sorbent tube followed by desorption into the GC oven. This system is advantageous because very large sample volumes can be tested (lakes, streams) to yield sub part per billion detection limits. Also surfactant laden samples can be analyzed with the spray and trap without any expected foaming problems.

MM-1 Strategy

The ability of the MM-1 to perform a wide variety of analytical measurements is accomplished be incorporating the various sample inlet devices and utilizing the mass spectrometer detector system. Sample preparation and analysis is conveniently simplified with the inlet devices. The mass spectrometer detector provides the capability to unambiguously identify organic compounds which are introduced into the detector. Table 2 lists the various MM-1 configurations which can be used to detect the organic compounds of interest. For example, volatile organic compounds can be analyzed in water by purge and trap GC/MS analysis. PCBs can be rapidly analyzed in soil by direct thermal desorption/MS with absolutely no sample preparation.



Table 2. MM-1 Strategy

Matrix	VOA Med DQO	VOA High DQO	SVOA Med DQO	SVOA High DQO
Air	CAA	Trap GC		
Water	CAA Headspace	P&T/S&T	Direct Thermal Desorption	Solvent Extraction
Soil Sediment Solid Waste	CAA Headspace	Solvent Extraction/ P&T/S&T	Direct Thermal Desorption	Solvent Extraction

DQO - Data Quality Objective

CAA - Continuous Air Analysis (probe)

P&T - Purge and Trap (GC)

S&T - Spray and Trap (GC)

Proven Performance with the MM-1

1990 Superfund Innovative Technology Evaluation (SITE) Program Demonstration²

During the summer of 1990, a complete and comprehensive study was conducted to evaluate the performance of the MM-1 as an alternative to technologies currently employed (stationary laboratory mass spectrometry) in the characterization of contaminants at Superfund Sites. The SITE Program evaluation included five indicators of data quality: Precision, Bias, Completeness, Representativeness, and Comparability.

In order to demonstrate the flexibility of the MM-1, three different modes of operation were performed which included VOCs in water, PAHs in soil, and PCBs in soil.

The analysis of VOCs in water is very similar to that of the EPA Method 624. Sample preparation involved a purge and trap followed by full scan GC/MS analysis. Single ions and reference internal standards are used for quantitation. A 25 minute analysis time is recommended which enables full separation of analytes prior to detection.

The analysis of PAHs in soil involves a simplified micro-extraction of the soil sample with an organic solvent. The Combination Air/Surface Probe with a short 3.5 meter capillary column is used for sample introduction with a 10 minute analysis time. Full scan acquisition is performed. Single ions and reference internal standards are used for quantitation as described in Method 8270.

The analysis of PCBs in soil represented the simplest analytical procedure. Unique multiple ions are monitored (MIM) for PCB

congeners on a real time basis. Following a simple 2 minute microextraction of the contaminated soil, a quick 400 second analysis is performed whereby PCB congeners are separated using the short 3.5 meter probe. PCBs are identified and quantitated by MIM.

These methods of analysis resulted in a high level of data quality which were in good agreement with the confirmatory Contract Laboratory Program GC/MS method results. The success of the EPA SITE demonstration establishes a high degree of confidence in the data generated with the MM-1. This in turn allows a user to take advantage of the unique features of the MM-1 so that it can be easily used to effectively complete a wide variety of analytical measurements.

Applications and Uses

US Army

The MM-1 is the only tested and accepted mass spectrometer system used by the military. It is mounted into the NBCRS Fox vehicle and is used for the detection of live chemical agents which may be used under hostile warfare conditions. During Desert Storm more that 60 NBC vehicles were used on missions to conduct around the clock monitoring for the presence of chemical warfare agents.

With the cold war over and no immediate military threat, the US Army has started using a number of their FOX vehicles with the MM-1 to perform analytical measurements of environmental pollutants and chemical munitions at their own military bases. This allows the soldiers to continue to train on the MM-1 and the FOX vehicles, and at the same time perform environmental assessments of the bases.

The MM-1 has been used at Dugway Proving Ground, Utah during a stand-off evaluation of different air purification systems. The MM-1 was set up for remote monitoring of the presence of breakthrough chemical agents at the discharge of the purification systems in order to determine how well each system performed.

The Chemical Research, Development and Engineering Center, DGP, MD., has a mobile laboratory with several MM-1s. They are involved with monitoring contamination such as munitions, chemical agents, and other environmental pollutants at military bases. They conduct environmental assessments of buildings and land to include health and safety risks and air/soil/water analysis.

State Agencies

State agencies such as the Dept. of Natural Resources and Environmental Control of Delaware provide 24 hour emergency response services for the state. With the MM-1 as a focal point of their mobile laboratory, analytical capabilities include rapid response for performing analytical measurements of air, soil, and water samples to determine the extent of contamination. DNREC performs perimeter air monitoring to identify and delineate noxious odors which have been reported to their office from the community. They also analyze contaminated soil and water samples resulting from accidents such as overturned vehicles, spills or leaks.

Fire Brigades

Several European fire brigades use the MM-1 while fighting fires. With health and safety in mind, the MM-1 gives fire fighters immediate information about not only the type of hazardous chemicals which may be present but also the extent in which they have migrated. Pollutants that are airborne can be measured on a real-time basis. Water that is used to extinguish a fire can be quickly tested to determine if the run-off water is contaminated which may pollute the public water supplies.

Environmental Management Firms

Satterthwaite Associates, a consulting firm, uses the MM-1 to perform environmental assessments of properties during land transfer, as well as property which is going to be newly developed. The MM-1 gives them the advantage of analyzing a large number of soil samples quickly to obtain unambiguous results on a real time basis in order to meet demanding deadlines of property transfers and environmental due diligence.

Environmental Resources Management Inc., has incorporated the MM-1 technology and offers a service which they name ERM-FAST (Field Analytical Services Technology). Using the MM-1, their mobile laboratory offers a wide range of mass spectrometric analyses providing their customers with an inexpensive alternative to laboratory analytical services. Additionally, the ability to work with the drilling crew allows an accurate guidance to additional sampling points and avoids unnecessary sampling of areas which have been quickly analyzed and found to be clean.

Science and Technology Corporation in Tooele, Utah uses an MM-1 to quickly assess the extent of VOC, SVOC, hydrocarbon, explosives, PCB's, and chemical warfare agents at many sites.

Conclusion

It has been shown, through numerous demonstrations involving a direct comparison of results generated with the MM-1 to data generated from similar conventional analytical techniques, that the MM-1 can be used to provide data of acceptable quality for a variety of data quality objectives. The MM-1 is the most advanced technique providing unambiguous identification, high sensitivity, and reliable quantitation, for rapidly evaluating hazardous waste sites at a lower cost than established CLP methods, or other existing field analytical capabilities.

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UNITARY AGENTS: A ROADMAP TO CONTROL LIMITS AND ANALYTICAL METHODS

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ABSTRACT

Why should we bother with control limits or additional analytical methods for chemical agents? There are a lot of reasons not to do anything. It's extremely controversial; very technically complex; we've never needed them in the past. However, just because the issues are difficult, doesn't mean they can, or even should, be avoided forever. So lies the problem of developing practical control limits and subsequent analytical methods for chemical agents for media other than air. The R&D efforts and application of such guidelines and methodologies for their use in drinking water, soil, milk, and unprocessed food items are reaching a critical stage among several scientific organizations, well beyond the Department of Defense. Such techniques will be absolutely imperative for contingency planning/execution associated with chemical demilitarization of both stockpile and non-stockpile surety materials. In the realm of treaty verification and clean-up efforts in the Unified Republics and third world nations, such procedures are a must. Even in our own nation, the implications of construction site clearance and installation restoration activities at current Army facilities is very real. By using existing toxicology data and employing currently established methods for incorporating health risk into the criteria-setting process, a first cut has been made at developing agent control limits for general population exposure. It is felt that this type of guideline-setting effort will be a driver for lowering limits of detection in existing analytical techniques. Knowing, however, that there are greater or lesser degrees of conservatism that permeate the scientific community, the assumptions and procedures for arriving at this initial proposal are presented to serve as a starting point in this very important effort.

UNITARY AGENTS: A ROADMAP TO CONTROL LIMITS AND ANALYTICAL METHODS

INTRODUCTION.

The purpose of this paper is to put forth some suggested approaches for assessing the environmental health risks associated with exposure to unitary agents in media other than It is intended that these proposed control limits be for evaluating the health risks to the general public. The authors admit up front that what you are about to read is fraught with assumptions, their own biases, and with some very real data gaps for making recommendations. It is felt, however, that although this issue is very controversial, and from a scientific point of view, is extremely complex, time is becoming a critical factor. The Army must act decisively to dedicate the necessary R&D resources to establish protective, yet pragmatic approaches to the chemical demilitarization effort, certain aspects of treaty verification associated with chemical surety materials (CSM), and to similar types of installation restoration activities. In all such scenarios, aspects of contingency planning must integrate relevant control criteria, viable analytical methods capable of reliably measuring these guideline concentrations, and the necessary restoration technologies available to clean up contaminated areas to an environmentally safe level.

WHY ARE CSM A PROBLEM?

There are several aspects of unitary agents which are currently coming under public scrutiny. Certainly, the most visible are those concerted efforts being directed at the demilitarization of the chemical stockpile. With the end of Desert Storm, and the fall of the USSR, the concerns over treaty verification as it relates to chemical weapons has also been prominent in the press. Further, the military-unique nature of chemical agents has caused the Army to reflect on such problems as construction site clearance and installation restoration in the vicinity of past manufacturing, storage, or test facilities. Additionally, the reentry/restoration contingency planning necessary to fully address potential accidental releases from any of these activities has brought into focus certain data gaps associated with pragmatic, scientifically responsible solutions to these scenarios.

PROPOSED CONTROL LIMITS/GUIDELINES (Watson et al. 1992).

Background.

a. To date, control limits for public exposure to unitary agents have been established for atmospheric concentrations as presented in the Table 1 (Watson et al. 1992). These ambient air control limits were finalized in 53 Federal Register 8504 (15 March 1988) and are not an issue here. The current analysis builds on previous work to calculate estimates of control limits for ingestion and dermal exposure to potentially contaminated drinking water, milk, soil, and unprocessed food items.

Table 1. Maximum agent control limits recommended by the Surgeon General's Working Group

Agent	Workplace (8 h)	General Population (72-h Time-Weighted Average) (mg/m ³)		
	(mg/m ³)			
H/HD/HT	3 x 10 ⁻³	1 x 10 ⁻⁴		
GA/GB	1×10^{-4}	3×10^{-6}		
VX ²	1×10^{-5}	3×10^{-6}		
Lewisite	3×10^{-3}	3×10^{-3}		

¹Values recommended by Surgeon General's Working Group after review of pertinent data and documented in Federal Register, 52:48458 (December 22, 1987). Final promulgation in Federal Register, 53:8504 (March 15,1988).

Notice and request for public comment on VX values in Federal Register, 52:19926 (May 28, 1987). Control limits recommended by the U. S. Department of Health and Human Services to the Secretary of the Army in October 1987. Final promulgation in Federal Register, 53:8504 (March 15, 1988).



Table 2. Existing and proposed field standards for chemical agents in combat drinking water

standard (µg/L)*	5 L/day intake	0.6 - 1.2	0.6 - 1.2	0.6 - 1.2	9.4 x 10 ⁻³	Not addressed
Suggested adult civilian standard (µg/L)*	2 L/day intake	1.5 - 3	1.5 - 3 ^t	1.5 - 3	2.3 x 10 ⁻²	Not addressed
	15 L/day intake	4¢	4*	*4	Under development ^h	Under development ⁸ Under development ⁸
Proposed combat stand	5 L/day intake	12°	12°	12°	Under development ^h	Under development ⁸
Existing combat standard $(\mu g/L)^*$ Proposed combat standard $(\mu/L)^{**}$	5L/day intake	20°	20°	204	200€	2000
Existing con	Agent 51	GA	GB	ΛX	Sulfur mustard	Lewisite (L)

*Assume combat drinking water contains no other toxic materials and that period of consumption does not exceed 7 consecutive days.

Not yet finalized; standardization will require establishment of acceptable risk levels by Offices of Surgeon General of Army, Air Force and Navy. Assumes 50% depression of RBC-ChE.

Derived in current analysis.

⁴U.S. Department of the Army 1986.

'Daniels 1988; calculated maximum permissible concentration (MPC) based on estimated human ChE_{so} threshold for GD drinking water exposure. GD considered to pose greater threat to military personnel than GA, GB, or VX because of GD's ability to quickly and stably bond to ChE ("aging"; makes ChE resistant to therapeutic reactivation) and its potency as a ChE inhibitor. Though VX is a more potent inhibitor, it is not as cumulative.

The estimated no observable adverse effect level for infants (see Watson et al. 1992 for exposure assumptions) are 1.4 x 101 µg/L (body burden of 0.43 µg/d). Ward 1970; Headquarters, U.S. Department of the Army 1982, 1986. Recommended MPC for consumption period in excess of 7 days is $50\mu g/L$.

"Available data on vesicant agent oral toxicity in laboratory rats and rabbits currently under study by agencies of the Army, Air Force and Navy.

The estimated no observable adverse effect level for infants (see Watson et al. 1992 for exposure assumptions) is 2.2 x 10³ µg/L.

Drinking Water. At present, the DoD allows the following maximum concentrations of chemical agents as field drinking water criteria (See first column Table 2). These criteria are applicable for short durations (<7 consecutive days), and assume exposure only to healthy adult combat personnel between the ages of 18 and 45. As such, these combat drinking water standards are not comparable to occupational or general population limits.

a. Nerve agent. Those criteria developed for the special military population may not be protective enough to be applied to the general population. By incorporating consideration for daily water consumption, compromised individuals, and threshold RBC-ChE depression, the existing and proposed field drinking water standards can be modified to yield estimated general population control limits as presented in Table 2 (Watson et al. 1992).

It should be noted that in addition to the actual nerve agents themselves, there is at least one hydrolysis product of VX, S-[2-(diisopropylamino)ethyl] methylphosphonothioc acid, that is also an anticholinesterase compound with toxic properties similar to that of VX (Aaron and Szafraniec, as cited in Yang et al. 1990). This analysis recommends that this compound be subject to the same drinking water control limits as VX. It does raise the issue that degradation products from all unitary agents should be scrutinized in the R&D arena to characterize yield and toxicity implications.

- b. Mustard agents. There exists a documented, semiquantitative method (Watson and Griffin et al. 1989) that utilizes EPA's Risk Assessment Guidelines for estimating the cancer risk to sulfur mustard exposure. This approach makes use of the "Rapid Screening of Hazard (RASH)" method, which provides results that compare favorably with findings of the traditionally used review process as practiced by committees such as EPA-CAG (the Carcinogen Assessment Group of the U.S. EPA), the ACGIH (American Conference of Governmental Industrial Hygienists), and the EPA Criteria Document Committees (Jones et al. 1988). The RASH relative potency approach includes the following protective assumptions:
 - daily intake at these levels for a 70-year lifetime

- no mitigation to reduce exposure

- no agent degradation for the period of exposure

- ingestion absorption coefficient of 1.0

- target excess lifetime cancer risk of 1 x 10⁻⁵

Application of the RASH method to sulfur mustard toxicity (Watson et al. 1989) relative to that of benzo(a) pyrene has resulted in control limit concentrations of 2.3 x $10^{-2}~\mu g/L$ and 9.4 x $13^{-3}~\mu g/L$ for adult water ingestions of 2 L/d and 5 L/d respectively. Application of the mass and water ingestion values for infants generated the mustard control limit of 2.2 x $10^{-3}~\mu g/L$.

b. The unitary stockpile contains nerve and vesicant agents in a variety of munition forms (Carnes 1989). The control limit analysis considers both nerve and vesicant agents and makes no distinction between liquid, aerosol, or vapor releases.

Biological Endpoints.

- a. Nerve Agents. While field-observable threshold effects to the eye are commonly used for early diagnosis of agent exposure (miosis for organophosphate (OP) nerve agents, and conjunctivitis for vesicants), an acute eye effects threshold cannot be considered sufficiently protective for the general public. As such, the proposed biological end point of red blood cell cholinesterase (RBC-ChE) depression at some value less than 20% is considered for determining the nerve agent control limit.
- b. Vesicants. As far as vesicants are concerned, the emphasis in the ensuing discussion will focus on sulfur mustard, since the amount of Lewisite and the associated hazards are less than that for sulfur mustard. In this regard, sulfur mustard is a known human carcinogen. It is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (Saracci 1981), as a Class 1 carcinogen by the National Toxicology Program (NTP 1989), and as a Class IA Toxic Air Pollutant ("Known Human Carcinogen") under the Code of Maryland Regulations (Title 26, Department of the Environment, Subtitle 11, Air Quality; BNA 1990). These classifications represent consensus that there is sufficient evidence to support a causal relationship between agent exposure and human cancer induction. And while EPA postulates a no-threshold effect for carcinogens and considers that any exposure has carcinogenic potential, the scientific community has employed risk analysis for addressing real world exposures. In 1990, the State of Maryland codified an acceptable cancer risk as follows:

"Insignificant risk concentration" means a concentration of a Class I toxic air pollutant in the atmosphere that would result in an excess individual lifetime cancer risk of not more than 1 in 100,000 (1 x 10⁻⁵) assuming continuous exposure for 70 years and using procedures consistent with EPA's Risk Assessment Guidelines. {Code of Maryland Regulations, Title 26.11.15 Part .01A(8)}

Thus, for the purposes of this discussion, the biological end point for calculating a dermal or ingestion control limit for sulfur mustard will be a 10⁻⁵ additional risk of delayed cancer induction.

Milk ingestion. Milk consumption among humans is maximal at 5 to 6 months, after which it declines with introduction of solid foods into the diet (ICRP 1975). Since infant agent control limit estimates for drinking water are based on a more protective consumption rate, the infant control limit estimates for water can be used interchangeably as an estimated no adverse effect level for milk. These calculated control limits for milk are presented in Table 3. Existing analytical capability cannot reliably detect agent in milk at these calculated control limits; thus alternative procedural strategies may be warranted. See Watson et al. 1992, pp. 19-20, for a more detailed discussion of these procedural contingencies.

Food ingestion. The RASH method previously referenced can be applied to the problem of estimating agent control limits for unprocessed foodstuffs, such as garden produce, that may be contaminated with nerve or vesicant agents. Details of the analysis can be found in Watson and Monro (1990), and the calculated guidelines are summarized in Table 3. Again, it is not clear that existing analytical capabilities can reliably detect chemical agents in foodstuffs at the calculated control limits. Is it that existing analytical protocols are not in place to reliably detect at these concentrations (i.e. sufficient concentration of the analyte), or is the instrumentation not sufficiently sensitive? As such, alternate decision-making strategies involve monitoring the ambient air concentration for comparison to the 8-hour time-weighted average for human workers, and destroying the crops in an environmentally sound manner if that value is exceeded. Open burning is not recommended due to the risk of agent revolatilization and downwind spread.

Soil ingestion.

- a. Nerve agents. VX is the only nerve agent of sufficient persistence to be a reasonable candidate for soil ingestion exposure. As described in Watson et al. 1992, by using the no-adverse-effect adult body burden for nerve agent is 6 $\mu \rm g/d$, then an adult consuming 100 mg/d of soil uniformally contaminated at 60 $\mu \rm g/g$ should exhibit no adverse effects. Similarly, with adjustment for body mass, a normal toddler could consume soil at 1.5 $\mu \rm g/g$, and a pica toddler could consume 1.7 x 10^{-1} $\mu \rm g/g$.
- b. Mustard agents. Using the RASH procedure as before, but with substitution of soil ingestion assumptions, guidelines for soil containing mustard can be calculated as presented in Table 3. However, since the analytical detection level of mustard in soil is 2 μ g/g, the excess lifetime cancer risk estimates for children exceed 1 x 10⁻⁵. As such, for ingestion as the exposure route of concern, adults (>18 years) could be permitted into an area of soil contaminated with sulfur mustard at the detection limit of 2 μ g/g if they take precautions against mouthing behavior (i.e. smoking, eating, etc.). All other groups (teens, toddlers, children, and pica children) should not be allowed into an area potentially contaminated with mustard at concentrations > 2 μ g/g.



Table 3. Summary of estimated agent control limits for various media (Watson et al. 1992)

[Being reviewed by Office of The Surgeon General, and will be reviewed by the Centers for Disease Control (DHHS), and Office of the Assistant Secretary of the Army (Installations, Logistics and Environment)]

			1	
Soil Dermal Exposure	(#g/g) Not applicable	Not applicable	1.5 (Assumption 1)° 8.5 x 10°2 (Assumption 2)°	4.7 x 10 ⁻¹ (adult) 1.1 x 10 ⁻² (Assumption 1)c ^e 1.1 x 10 ⁻² (normal 6.0 x 10 ⁻⁴ (Assumption 2) ^e toddler) 1 x 10 ⁻³ (pica toddler)
So	(Ag/g/u) Not applicable	Not applicable	60 (adult) 1.5 (normal toddler) 1.7 x 10 ⁻¹ (pica toddler ⁴)	4.7 x 10 ⁻¹ (adult) 1 1.1 x 10 ⁻² (normal toddler) 1.1 x 10 ⁻³ (pica toddler)
Unprocessed Produce		0.02 - 10 ppb*	0.02 - 10 ppb*	1.5 x 10 ⁻² $\mu g/kg$ (adult) ^b 4.5 x 10 ⁻³ $\mu g/kg$ (infant)
Milk ($\mu g/L/d$)	1.4 x 10 ⁻¹ - 2.9 x 10 ⁻¹	1.4 x 10 ⁻¹ - 2.9 x 10 ⁻¹	0.6 - 1.2 (adult) 1.4 x 10 ⁻¹ - 2.9 x 10 ⁻¹	2.2 x 10³
$(\mu g/L/d)$	5 L/d intake 0.6 - 1.2 (adult)	0.6 - 1.2 (adult)		9.4 x 10 ⁻³ (adult) 2.2 x 10 ⁻³
Drinking Water (μg/L/d)	2 L/d intake 1.5 - 3.0 (adult) 1.4 x 10 ⁻¹ - 2.9 x 10 ⁻¹ (infant)	1.5 - 3.0 (adult) 1.4 x 10 ¹ - 2.9 x 10 ¹ (infant)	1.5 - 3.0 (adult) 1.4 x 10 ⁻¹ - 2.9 x 10 ⁻¹ (infant)	2.3 x 10 ² (adult) 2.2 x 10 ³ (infant)
	GA	GB	××	Sulfur mustard

"Depends on produce item in question (e.g., grains at 0.02 ppb and kiwi fruit at 10 ppb).

Average value for entire dietary intake; based on excess lifetime cancer risk of 1 x 105.

'See Watson et al. 1992 for assumptions underlying these estimates.

^dPica toddler is defined as toddler with a pathological appetite for soil.

Dermal exposure to soil. At present, there are insufficient data on transfer factors for VX and mustard in soil to skin to perform a direct estimate of control limits governing soil dermal exposure. Two alternative procedures have been put forth (Watson et al. 1992) to address this issue.

- Assume that the maximally exposed individual would absorb no more agent through the skin than via ingestion. Thus the estimated control limits for soil ingestion could be used interchangeably as control limits for dermal exposure to soil. The resulting control limits for any soils that may come in contact with the skin would be 1.5 μ g/g for VX, and 1.1 x 10⁻² μ g/g for sulfur mustard agents.
- Assume that the maximally exposed individual would absorb through the skin no more than 50% of that absorbed by a pica child. The usual soil ingestion rate for a toddler is 590 mg/d. The resulting control limits for any soil that may come in contact with the skin would be 8.5 x 10^{-2} μ g/g for VX, and 6.0 x 10^{-4} μ g/g for sulfur mustard agent.

Data gaps. As can be seen from the previous analysis, there are many informational voids in the calculation and development of these control limits. Two of the most pressing areas of consideration involve needed toxicology studies on the agents materials themselves, as well as their degradation products, and extensive developmental efforts directed at the analytical methods, particularly the detection level.

While adoption by the Office of The Surgeon General of even some interim control limits for the various environmental media would be a viable driver for analytical methods development, there remain the problems of having an established surety laboratory in which to conduct this development, and technical issues associated with low-level detection. New methodology may have to be utilized in order to reach the low detection levels which will be dictated by the control limits.

Another area of concern involves the toxicology studies that are available with which to establish control limits. While the human volunteer studies conducted during the 1950s and 60s are definitely a thing of the past, there still are major holes in the available information. Such data gaps necessitate the use of techniques such as RASH to make a first cut at control limits. But even on those studies that have been completed, there remains some question as to their completeness in light of current requirements for "good laboratory practice" and study documentation in general. Again, the requirement for such

studies to be conducted in a surety laboratory is a complicating factor. However, the objective of these investigations should be to develop toxicological, environmental, and analytical data on CSM and their degradation products. This information would be used to support health risk assessments criteria for construction site clearance and installation restoration activities at contaminated sites. Such studies would validate or at least update initial estimates for control limits. Table 4 is a first cut at the types of studies that should be available to make more informed decisions. Also see Watson and Griffin 1992 for a more detailed discussion of CSM toxicology studies.

ANALYTICAL METHODS.

Sensitive detection methods have been established for airborne monitoring, since all current exposure criteria are based on airborne concentrations. At present, GC-based methods such as bubblers, DAAMS, or minicams are in use in surety laboratories, depots, and the JACADS. Modern field monitors based on ion-mobility spectrometry (IMS) have recently been fielded as chemical-agent monitor (CAM). The CAM can detect airborne concentrations above the immediately dangerous to life and health (IDLH) levels, but cannot be used to establish TWA The NBC recon vehicle, fielded during Desert Storm has an on-board GC/MS denoted the MM-1 mass spectrometer. vehicle is a mobile chemical laboratory that will be at the center of any emergency involving release of chemical agent. MM-1 will be able to analyze actual agents after extraction from soil or other media. However, standard extraction methods are still done on a case-by-case basis. One area where future research is needed is analysis of degradation products of the agents. The degradation products are typically ionic, and cannot be detected even by sensitive GC/MS such as the MM-1. This is especially acute in the case of VX, where one product from the hydrolysis of VX has been shown to be almost as toxic as the agent itself (Watson et al. 1992).

For some organophosphate nerve agents, further development will be needed to quantify low levels of VX and GB in the various environmental media. Additionally, field screening methods to support field operations are lacking. Chemical sensor technologies need to be evaluated. Remote or "in soil" sensors using fiber optics, piezoelectric, electrochemical, and biological sensors offer possibilities for on site in-situ determination of contamination. CSM related immunoassays (Hunter 1982, Erhard 1989) have been evaluated, and have been adapted for use as chemical sensors.

Table 4. Toxicity assessment studies for CSM (Wentsel 1992)

Health Effects

Acute Toxicity (Oral, Dermal, Inhalation)

LD_{5Q} (LOAEL, NOAEL, NOEL)

Irritation (eye, skin)

Mutagenicity

Gene Mutation

Chromosomal Aberration

Primary DNA Damage

Other Toxic Effects

Subchronic (LOAEL, NOAEL, NOEL)

Metabolic/Pharmacokinetic

Structural Activity Relationship

Reproductive Effects

Teratogenicity

Carcinogenicity

Environmental Fate - Aquatic/Terrestrial

Transport/Transportation Bioconcentration/Bioaccumulation Standard Aquatic Fate Studies Standard Terrestrial Fate Studies

3X/5X ALTERNATIVES. The terms XXX (3X) and XXXXX (5X) were established to define specific levels of <u>decontamination</u> for items which have been subject to liquid contamination or long term vapor contamination (AMC Regulation 385-13, 1987):

3X indicates that the item has been surface decontaminated, bagged/contained, and appropriate tests/monitoring have verified that vapor concentrations above $0.003~\text{mg/m}^3$ for mustard agents, $0.0001~\text{mg/m}^3$ for GB, and $0.00001~\text{mg/m}^3$ do not exist. Monitoring is not required for completely decontaminated and disassembled parts made of essentially impervious parts.

5X indicates that an item is clean and may be released from government control without precautions or restrictions. Unlike the 3X level of decontamination, the 5X status is not currently associated with any concentration limits. What has been associated with the term 5X is instead a treatment standard -- i.e., maintenance at 1000°F for at least 15 minutes -- that will "completely destroy the agent."

While originally established for laboratory safety and decontamination of finite items (i.e., equipment), these terms are, perhaps incorrectly, being used to address environmental concerns and general public safety. Many of today's "scenarios" may require alternate definitions of what constitutes "safe and clean from chemical agent." Some of these scenarios include installation restoration, base closure, pre-construction clearance, demolition and disposal. In the case of chemical agent incident, reentry/restoration actions may also be hindered by the lack of set alternate standards.

There are several potential options to alternate standards (Weyandt, T.B., 1991) such as establishing a concentration limit for 5X, or reconsidering the levels associated with 3X as "clean" based on analyses of health risk or reassigning acceptable levels of decontamination based on material and future use. Unfortunately, one of the Army's biggest problems in setting alternate standards will be to overcome current perceptions associated with the infamous 3X and 5X terms. In this respect, new innovative methods and technologies are being sought to better (quickly and accurately) detect/monitor agent presence, predict/model agent adsorption, absorption, vaporization and stability under various conditions, and assess risk (both acute and carcinogenic).

Some problems with existing technologies and current studies are discussed below:

- a. Current detection methods/systems such as DAAMS or ACAAMS are generally set to monitor for one of two levels: the 3X levels (set for worker safety) and the general public limits (GPLs) for perimeter monitoring. While detection limits could be lowered by increasing the volume and rate of air flow, this would probably increase the inaccuracy of the systems. These systems generally err to the false positive due to interferences with other compounds in the atmosphere.
- b. Could GPLs be used as the 5X concentration standard? Using health assessments it may be possible to confirm/adjust these concentrations.



- c. A recent health risk assessment (Watson, A.P. et al., 1989) was a pioneering effort in quantifying the health (carcinogenic) risk associated with low (3X) concentrations of mustard agent. While the study revealed risks slightly higher than general EPA standards, several very protective assumptions were used. Additional data (to eliminate/reduce certain assumptions) and refinement of the assessment techniques are necessary in establishing alternate 5X standards.
- d. A study into the likelihood of off-post chemical agent contamination (U.S. Army Chemical Research, Development and Engineering Center (CRDEC), 1992) using a modeling approach indicates a possibility of low agent concentrations near some installations. This assessment did not address contact hazard of agent to wood, metal or vegetation, and therefore does not thoroughly address the health risks involved with all routes of exposure. The modelling also does not address the carcinogenic potential of mustard agent. The CRDEC memo report is currently undergoing review, and is not considered an official Army position.
- e. Biomonitoring using ChE activity is being pursued as a method of identifying nerve agent presence in the event of an incident or release (Halbrook et al. 1992). Domestic sheep have been identified as potential "field monitors" due to their low natural variability in ChE activity and tractability.
- f. Currently, the State of Utah has made the decision that all 3X and 5X material will be, by definition, hazardous waste. The U.S. Army Test and Evaluation Command (TECOM) (1992), in an effort to support work at Dugway Proving Ground and Tooele Army Depot, is submitting a delisting petition to the State of Utah for 3X and 5X waste. The petition is based on the characteristic tests which are used to identify a HW -- if the waste is submitted for these tests and does not fail, then it is not hazardous. According to TECOM sources, the status seems favorable.
- g. AMC Regulation 385-131 states that material decontaminated to the 3X level may be disposed of in an EPA-approved (i.e., RCRA) landfill. How will the TECOM delisting petition affect this policy?
- h. Current options for the APG pilot plant include incineration or surface decontamination, air-monitoring to 3X level, and disposal in a RCRA landfill (if allowed by the State of Maryland). One obvious problem with this approach is decontaminating the building material. Little knowledge is available about the adsorption/absorption of agent on brick, cement, wood and other porous materials. How long should air monitoring continue? Should the building be subject to various conditions (e.g., heat) when air monitoring?

- i. The current treatment standard for 5X is not always an acceptable process. Materials/equipment that may be reused are destroyed during incineration. In the case of structures, incineration can only be a disposal option. How then can we address issues of reentry and restoration?
- j. In a very recent policy document (U.S. Department of the Army 1992), a major first step was taken. As of 15 April 1992, alternate 5X definitions may be used in agent operations. While alternate 5X definitions are now acceptable Army policy, the Department of Defense Explosive Safety Board (DDESB) must approve any proposed method that can detect below "no-effects" levels. The Army has now stated that it is possible to get redefined 5X limits, once no-effects levels are established. It now becomes essential that CDC/OTSG determine "no-effect levels" as proposed in Watson et al. 1992, or by whatever means available so as to be protective of health and the environment, so that alternate 5X criteria can be implemented.

TREATMENT TECHNOLOGIES.

To date, most of the attention associated with treatment of CSM has focused on the demilitarization of the chemical stockpiles (SANA, 1991). Primarily, the technologies under consideration have been chemical neutralization and incineration. Little, if any, R&D has been directed at clean up and remediation This is particularly bothersome when, at the very least, the Army will have to address the remediation at those installations which will be disposing of the agent stockpiles. Will that action be a follow-on to the chemical demilitarization effort, or will that be an installation restoration activity? Can soil be burned (incinerated) to clean up agent contaminated sites, the same way that explosive contaminated sites have been treated? Are there other technologies that are as efficient as incineration, but considerably less costly? There are currently some remediation treatment technologies that are receiving consideration (Watson and Munro 1990). These include:

- Bioremediation
- Hot air gasification
- Incineration
- Chemical neutralization
- Weathering with quarantine
- Liming flyovers (looking at ammonia as an alternate to lime)
- Photodecomposition

The remediation program, in the Army at least, has evolved from the treatment of solvent/gasoline contaminated groundwater, to the treatment of explosive contaminated sites. Perhaps the trend



toward CSM contamination may be the next logical step. Not that this is by any means a ubiquitous problem in the DoD, but at those installations where it does occur, the difficulties (be they perceived or real) associated with clean up will be considerable. Although CSM remediation may seem like a problem unique to the military, this is not necessarily the case. There is extensive practical experience in dealing with OP pesticide HAZMAT incidents that would provide valuable information. Interaction with the pesticide professional community could be very insightful in addressing CSM remediation issues in the future.

SUMMARY. The information contained in the paper covers a very extensive breadth of subject material. The intent of this discussion is not to provide a comprehensive analysis of the various topics, but rather is an attempt to focus attention on the R&D areas that need to be addressed as they relate to CSM. Some of the most pressing applications related to chemical agents include:

- Chemical demilitarization
- Treaty verification
- Installation restoration
- Construction site clearance
- Reentry/restoration activities

A key focus within this document are the proposed guidelines for unitary agents that were put forth by Watson, A.P. et al.,1992, as presented in Table 3. Inherent in the derivation of these control limits were the scientific data gaps that exist, and the use of the "Rapid Screening of Hazard (RASH)" method to generate a starting point for guidelines in light of these deficiencies. It should also be pointed out that, in addition to the actual surety materials themselves, there are several degradation products that need to be evaluated with an eye toward their toxicity, and the resulting implications.

Another important message of this analysis is, in the formulation of control limits that could be accepted by CDC/OTSG, that such acceptance would be the driver for the R&D efforts associated with analytical methods. This is especially true in environmental media other than air, (i.e. drinking water, soil, milk, and foodstuffs).

A critical issue related to several of these CSM applications is whether the decontaminated material resulting from these operations is classified as a hazardous waste. Without improved analytical capabilities and an improved understanding of health risk as it relates to 3X/5X material, there remain major roadblocks to a pragmatic resolution of clean up efforts.

And finally, there is a dire need for expanded R&D efforts for CSM treatment technologies. In the installation restoration arena alone, the Army has evolved its capabilities from the solvent- gasoline scenario to instances of explosives in groundwater. Following this pattern of emphasis on military-unique formulations, it is only a matter of time before methodologies capable of cleaning up CSM and their degradation products are required. Interface with the commercial pesticide industry could provide valuable technology transfer and extensive practical experience. While prove out of such technologies will take some time to develop, the Army would do well to initiate action now rather than have external mandates imposed at a later date.

The issues raised by this discussion are serious. The proposed control limits, as well as the emphasis on analytical techniques and treatment technologies is only meant to draw attention to all environmental aspects of CSM, and serve as a starting point for future discussions. It is clear, however, that if this document is to function as a roadmap for finding solutions to these problems, that the highway for success must pass through the R&D community.

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REVIEW OF CURRENT AND POTENTIAL FUTURE SAMPLING PRACTICES FOR VOLATILE ORGANIC COMPOUNDS IN SOIL

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ABSTRACT

This study compares two sampling and handling methods for the collection of soils to be analyzed for volatile organic compounds (VOCs). One method, which may be incorporated into future protocols, uses a simple subcoring device that allows set volumes of soil to be removed rapidly from the surrounding substrate and transferred to a tared analysis vessel, that a) can be analyzed via needle-septum puncture, b) attaches to a purge-and-trap system, or c) contains methanol. This less disruptive method not only limits mechanical fracturing during collection and lengthy sample exposure while transferring, but avoids soiling of the collection vessel seals. The findings show that, in order to acquire more accurate VOC concentrations in vadose zone soils, there is a need for limited disruptive and exposure practices.

INTRODUCTION

Recently, trichloroethylene (TCE) contamination was discovered in production wells at a U.S. Army facility. During the subsequent site investigation, several boreholes and monitoring wells were installed to define the extent of contamination. Under the supervision of the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), collocated soil samples were taken for chemical analysis. Collocated samples should not be confused with sample splits, the latter representing a sample that has first been homogenized (mixed), then sampled. The collocated subsamples were obtained by following the commonly accepted practice of filling a transfer bottle for shipping and subsequent contract laboratory analysis, and with a recently proposed limiteddisruptive and exposure method (T.M. Spittler, personal communication; Lewis et al., 1991), for on-site analy-

Current soil sampling protocols require that samples for the analysis of volatile organic compounds (VOCs) be shipped to the laboratory in bottles that have been filled to capacity (i.e., no headspace). Both the practice of filling bottles, and the removal of a portion after shipping, cause the soil sample to be disturbed. In addition, while filling the bottle the sealing surfaces are often soiled, compromising leak-free containment. Present guidelines limit storage time to 14 days and temperature to 4°C, while cautioning against cross contamination (materials; i.e., stainless steel spoons, glass bottles with Teflon closures, plastic-gloved hands). The guidelines, however, do not address the actual collection process, and thus fail to provide detailed descriptions of how soil samples should be handled in the field or transferred from the shipping vessel after being returned to the laboratory.

The proposed method of T.M. Spittler (personal communication) and Lewis et al., (1991), specifies a procedure for transferring soil subsamples that eliminates unnecessary intergranular disruption and exposure. In particular, their protocol states that disturbance of the native soil structure should be minimized, and that placement of subsamples should only be into a vessel from which it can be analyzed, or that contains a solvent. This can be achieved by using a simple coring device that allows small "plugs" of soil to be rapidly removed from the surrounding substrate and quickly transferred to a tared vial, which a) is analyzed by a needle-septum puncture, b) has an adapter allowing for direct attachment to a purge-and-trap system, or c) contains an extraction solvent such as methanol (MeOH). This method not only limits subsample disruption and exposure but avoids soiling of the collection vessel sealing surfaces, ensuring a leak-free closure. The objective of this study was to determine the effects that these two sampling and handling protocols have on the measured concentrations of VOCs in soil.

EXPERIMENTAL.

An outline of the two soil-sample collection and handling methods used and their effect on the concentration of VOCs present is discussed here. Detailed descriptions of the analysis procedures used on site and by the contract laboratory can be found elsewhere (Hewitt et al., 1991; Hewitt et al., 1992; Hewitt et al., under review).

Subsample Collection

A. Samples Collected for Contract Laboratory Analysis

The site investigators tasked with the collection of samples were requested to fill two 40-mL VOA vials

for VOC analysis. These narrow-mouthed vials (1.8-cm i.d.) were filled by transferring soil from the split-spoon sampler using a stainless steel serving spoon (≈3.5 cm dia.). Using this collection method, it took about one minute to fill each VOA vial, and left the vial's threads and sealing surface covered with grains of soil. Attempts were made to wipe these surfaces prior to capping; however, this was effective only for small soil aggregates; individual grains remained, as was apparent by the sound of glass scoring, upon tightening the caps.

B. Samples Collected for Analysis On Site

The collection method used for samples analyzed on-site followed the limit-disruptive and exposure technique of T.M. Spittler (personal communication) and Lewis et al. (1991). A 10-cc plastic syringe (1.6-cm o.d.) with the needle end removed (Fig. 1) was used to extract, isolate and transfer soil plugs (Fig. 2) from the split spoon into the collection vessel. The plunger was set so that between 2 and 3 cc of soil was retained in the cylindrical barrel. After wiping the external surface of the syringe, the soil plug was dispensed into the appropriate VOA vial by depressing the plunger (Fig. 2). A minimum of two soil plugs was extracted from each split spoon sampled, one for headspace gas chrom-

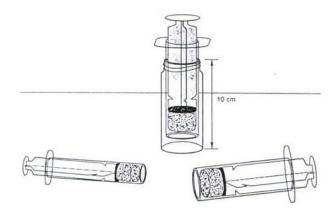


Figure 1. Illustration of five subsample soil plugs obtained with the coring device, for purge-and-trap analysis.

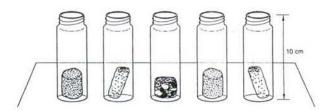


Figure 2. Illustration of 10-cc and 3-cc coring devices, and a 10-cc corer inside a 40-mL VOA vial.

atography (HS/GC) and the other(s) for purge-and-trap gas chromatography mass spectrometry (PT/GC/MS) analysis. Vials taken into the field were all tared and contained either 30 mL of Type 1 water (HS/GC), 20 mL of MeOH, or were empty. The empty vials were equipped with a modified purge-and-trap vial adapter (Associated Design Model PT-6005-0002) which allows for direct connection to a purge-and-trap system. The decision on whether to place the soil plug into the VOA vial containing 20 mL of MeOH or the empty vial was made in the field based upon readings taken from a PhotoVac (Photovac, Inc.) VOC hand-held probe. When readings of greater than 200 parts per million (ppm) total ionizable gases were observed, the vial containing MeOH was used, whereas for readings less than 200 ppm the empty vial was selected. Measurement of total ionizable gases was performed by sticking the sensor tip into a freshly created finger depression in the soil sample. All VOA vials were weighed after collection to determine the actual weight of soil (moisture included). Each subsampling took approximately 15 seconds, and, as can be seen in Figure 2, the majority of the soil plugs remained intact, showing little granular disruption, thereby minimizing exposure to the atmosphere prior to sealing the vial. Sealing surfaces remained clean, allowing for leak-free closure.

II. Transportation and Storage

A. Contract Laboratory Samples

The VOA vials filled for VOC analysis were surface wiped, recorded, custody sealed, stored and shipped at 4°C, and analyzed within 14 days of collection.

B. Samples Analyzed On Site

All soil samples were stored at 4°C. Aqueous extraction HS/GC samples were analyzed within two days and PT/GC/MS samples within 14 days of collection.

III. Laboratory Sample Handling and VOC Analysis

A. Contract Laboratory

Five grams of the soil were removed from the vial, weighed, and transferred to a sparge tube. Once connected to a sample purging system, 5mL of water with the appropriate surrogates were added and the sample analyzed by USATHAMA-certified method LM16, a PT/GC/MS analysis method that is similar to EPA SW-846, Method 8240 (Hewitt et al., 1991).

B. On Site

The subsample collection and handling method used allows for direct analysis of the vessels into which

Table 1. Trichloroethylene concentrations for collocated subsamples taken during the drilling of eight boreholes.

	Or	n-site	Contract Lab	
	*HS/GC	•PT/GC/MS	PT/GC/MS	
Sample	(mg/Kg)	en en 400 en 100 A 400 en 2000.	(mg/Kg)	
Borehole 1				
A	< 0.003	NA	**<0.0038	
В	< 0.003	NA	< 0.0038	
C	< 0.003	<0.003	< 0.0038	
Borehole 2		30.000	V0.0038	
A	< 0.003	NA	< 0.0038	
В	< 0.003	NA	< 0.0038	
C	< 0.003	< 0.003	< 0.0038	
Borehole 3			VO.0038	
A	< 0.003	NA	< 0.0038	
В	< 0.003	NA	< 0.0038	
C	< 0.003	< 0.003	< 0.0038	
Borehole 4			X0.0030	
A	0.20/0.11	0.14	0.014	
В	9.6	13.0	0.046	
C	130.0	33.0	0.095	
D	0.40	0.63	< 0.0038	
Borehole 5			10.0036	
A	2.5	2.3	0.020	
В	1.4	NA	< 0.0038/< 0.0038	
C	15.0	0.10	< 0.0038	
Borehole 6			10.0036	
A	< 0.003	NA	< 0.0038	
В	< 0.003	< 0.003	< 0.0038	
Borehole 7			0.0036	
A	< 0.003	NA	< 0.0038	
В	< 0.003	< 0.003	< 0.0038	
Borehole 8			V.0036	
A	1.6	3.6	0.016	
В	0.30	0.53	0.010	
C	0.58	0.82	0.20/0.19	
*HS/GC	Headspace gas chromatograph			
•PT/GC/MS	Purge-and-trap, gas chromatogra	aph, mass spectrometer		
NA	Not analyzed	• continue constituti • continue contin		
**	Method reporting limit			

the soil plugs were placed, or the analytes of interest are present as solutes in MeOH, a solvent from which VOCs are not easily lost. Analysis was performed by either HS/GC or by EPA SW-846, Method 8240 (Hewitt et al., 1992).

RESULTS AND DISCUSSION

The TCE concentrations found in soils are presented in Table 1. Included are the results reported by the contract laboratory (CL) and from on-site analysis. None of the values were corrected for soil moisture content, and those values supplied by USATHAMA via the contract laboratory will be processed further. The effects of using preliminary data have little influence on the interpretation presented.

Log-log plots of the soil TCE concentrations shown in Figures 3-5 represent all collocated samples where at least one method of analysis established a value greater than 0.0038 mg TCE/Kg (reporting limit

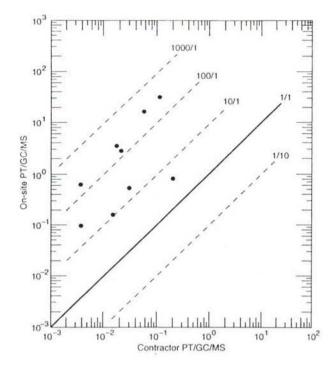


Figure 3. Log-log plot of collocated purge-and-trap trichloroethylene soil concentrations (mg TCE/Kg), as established by the contract laboratory and on site.

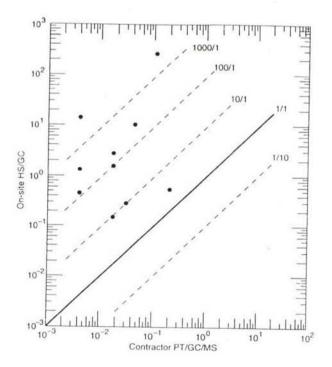


Figure 4. Log-log plot of collocated purge-and-trap and headspace-gas chromatography trichloroethylene soil concentrations (mg TCE/Kg) as established by the contract laboratory and on site, respectively.

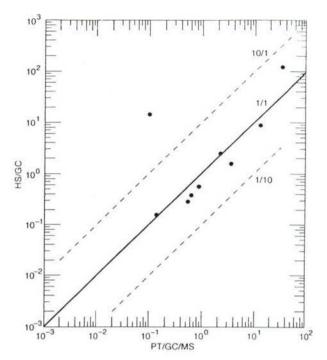


Figure 5. Log-log plot of collocated purge-and-trap and headspace-gas chromatography trichloroethylene soil concentrations (mg TCE/Kg) as established on site.

value). These figures include the axis of theoretical agreement (solid line), and order of magnitude intervals about this axis (dashed lines). By observing where the points fall in relation to the dashed lines one can see relative disagreement between the two methods being compared. Figures 3 and 4, both of which plot the results of the contract laboratory versus those obtained on site using PT/GC/MS and HS/GC, respectively, show that the majority of points differ by at least one order of magnitude, and frequently by two or three orders of magnitude. On an average basis, the disagreement approaches two orders of magnitude. Conversely, eight of the nine points shown in Figure 5, a plot depicting soils collected with the limited-disruptive and exposure method and analyzed by two different analytical methods, are within one order of magnitude from the theoretical agreement axis. Overall, the variation present in Figure 5 is well within the range of VOC analyte variability often encountered with environmental soil samples (Hewitt et al., 1992).

Linear regression analysis comparing the TCE concentrations for these above background values (>0.0038 mg TCE/Kg) established the following correlation coefficients: CL-PT/GC/MS versus on-site-PT/GC/MS, $r^2 = 0.0454$; CL-PT/GC/MS versus on-site-HS/GC, $r^2 = 0.0524$; on-site-PT/GC/MS versus on-site-HS/GC, $r^2 = 0.878$. Clearly, good agreement exists for collocated

Table 2. Results for trichloroethylene in groundwater samples.

	On-Site *HS/GC	•PT/GC/MS
Well Sampled	(mg/L)	(mg/L)
1	< 0.0001	< 0.0005
2	1.0	0.53
3	< 0.0001	< 0.0005
4 5	0.0047	0.0060
5	0.040	0.050
6	46.0	14.0
7	0.011	0.0059
8	1.4/1.5	1.2/1.1
9	160.0	64.0
11	3.2	1.5
12	0.29	0.18
*HS/GC •PT/GC/MS	Headspace gas chron Purge-and-trap, gas mass spectrometer	

subsamples when analyzed on site (valid at 99.9% confidence level). Results for the collocated subsamples collected by the site investigators using the currently accepted field sampling practices and analyzed at a contract laboratory do not correlate with the results obtained for those collected and handled by the newly proposed less disruptive and limited exposure procedure, and analyzed on site (Fig. 3, 4).

Two trends are apparent: 1) soil subsamples analyzed by the contract laboratory resulted in lower TCE concentrations than those analyzed on site; 2) soil subsamples collected with the limited-disruptive and exposure method and analyzed by either HS/GC or PT/ GC/MS (EPA, Method 8240) provided very similar TCE soil concentrations. The latter finding agrees with our earlier studies that have been documented elsewhere (Hewitt et al., 1991; Hewitt et al., 1992; Hewitt et al., under review). Since the focus of this paper is collection and handling practices, all possible explanations for the marked discrepancy for the interlaboratory results will be addressed. These include instrument calibration, biodegradation, analyte inhomogeneity, and subsample collection and handling.

A. Calibration Error

The results obtained for a round of groundwater samples analyzed by both the contract laboratory and on site are shown in Table 2. These water samples were collected by the site investigators two weeks after completing the installation of six monitoring wells (Table 3, wells 7-12). The other wells presented in this table are existing service wells. Here the method of analysis used by the contract laboratory was USATHAMA-certified method UM17, a method based on PT/GC/MS; HS/GC was performed on site. The results from the two laboratories are in much better agreement ($r^2 = 0.995$. Fig. 6) than was achieved for the soil samples (Fig. 3, 4). This water analysis comparison demonstrates that the departure in values for the TCE soil determinations between laboratories is most likely not a calibration problem. Additionally, the discrepancy between laboratories for the TCE soil concentrations was random, a pattern not attributable only to calibration offset (Fig. 3, 4).

B. Biodegradation Losses

Since aqueous extraction HS/GC is not a destructive analysis method (subsamples are not sacrificed), a subset of these samples was monitored over a

Table 3. Holding time study of sample subset stored at room temperature and analyzed by headspace gas chromatrography.

		*TCE m Holding					
Sample	1d	4d	8d	11d	15d	21d	25d
1	1.6	1.6	1.6	1.6		1.6	
2	16.0	15.0	15.0	_	15.0	_	15.0
3	130.0	130.0	130.0	_	_	130.0	15.0
•4	0.29	0.30	0.28	0.26	7-2	0.24	_
5	0.25	-	0.26	7	0.24	-	0.23
6	0.15	_	0.15	_	0.14	_	0.13

^{*}TCE.... Trichloroethylene

^{•4......} Increase in cis-1,2-dichloroethylene observed as the concentration in TCE decreased.

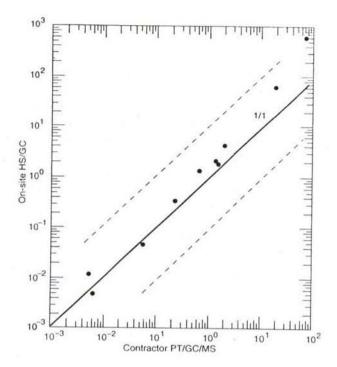


Figure 6. Log-log plot of purge-and-trap and head space-gas chromatography trichloroethylene ground water concentrations (mg TCE/mL) for first sampling round.

period of 21 to 25 days (Table 4). The soil subsamples selected were representative of the range of TCE concentrations observed, and include several taken near the surface where higher biological activity is anticipated. To stress potential effects, treatment between analyses consisted of room temperature (22°C) storage. Between analyses, vials were inverted so that the suspended soil settled onto the Teflon-lined septa. Little or no decrease in the TCE concentrations was measured as a result of this treatment. The sample with the greatest relative loss of TCE showed a corresponding increase in cis-1,2-dichloroethylene. Although this test does not duplicate the handling and storage conditions subjected to those samples sent for contract laboratory analysis, it provides strong evidence that rapid biodegradation of this highly chlorinated organic compound is unlikely, even for an extended holding period.

C. Sample Inhomogeneity

To address the problem of sample inhomogeneity, the collection of multiple subsamples is usually performed to assess analyte variability. The results in Table 5, for subsamples taken during the drilling of the groundwater monitoring wells, show that the inhomogeneity within a split spoon was small (threefold)

Table 4. Subsamples taken are listed from top of split spoon to bottom, bottom being the end of greatest depth. Number of samples collected from a split spoon dependent on the length of soil core retrieved.

	*TCE (mg/Kg) Individual Sample *HS/GC	Average and Std. Dev.
	0.042	
A.	0.035	0.038±0.004
	0.037	
	0.38	
В.	0.39	0.45 ± 0.12
	0.59	
	0.48	8
C.	0.50	0.76 ± 0.46
	1.3	
	0.29	
	0.27	
D.	0.21	0.22±0.07
	0.10	
	0.12	
	0.066	
	0.14	
E.	0.16	0.14±0.05
	0.17	
	0.18	
	25.0	
F.	24.0	25.0±2.0
	27.0	
	0.20	
	0.31	
G.	0.18	0.19 ± 0.07
	0.13	
	0.14	

*TCE.... Trichloroethylene

compared to the disagreement found between the two laboratories (tenfold to thousandfold). These subsamples were taken approximately every seven cm along the length of the split-spoon core with no visible discontinuities in the soil structure. This range of TCE concentration would not necessarily be representative of all split spoons, especially if a clay lens had been

penetrated. Other soil features that may influence VOC analyte distribution are grain-size distribution, soil type and structure, mineral type, and organic and moisture content (Chiou, 1989). However, since the boreholes were often in the near vicinity of these groundwater monitoring wells, and since analyte variability is often a random feature, it is very unlikely that the soil sampled by the site investigator always contained less TCE than the subsamples taken for on-site analysis.

D. Collection and Handling Method

Investigators (Siegrist and Jenssen, 1990; Lewis et al., 1991) have shown that sample disturbance can cause VOC losses up to 80%, relative to undisturbed controls. Laboratory evidence (significant at the 95% confidence level) exists for VOC losses when comparing subsamples that were transferred from one vessel to others that were either empty or contained a solvent (Jenkins and Schumacher, 1987). In addition, soiled threads and sealing surfaces of sampling bottles will contribute to VOC losses. To test this hypothesis, a simple test was performed looking at MeOH stored in VOA vials with and without grains (<0.2 mm dia.) of soil from this site smeared over the bottle's neck and threads, then wiped clean with a gloved hand, as had been observed in the field (soil grains = 0.06 g/bottle). The results showed that seven of ten soiled VOA vials suffered continuous weight loss while no weight loss was found from ten unsoiled vials. Thus, VOCs may be continuously lost from vessels when casually filled to capacity with soil.

Presented here is evidence supporting the concept that soil sample collection and handling treatments were the major factor responsible for the large discrepancy between the TCE concentrations reported by the two laboratories for the collocated soil subsamples. A major objective of a site investigation is to establish representative VOC contamination concentrations in soil. This objective can not be met if native soils are disaggregated causing fractures along grain boundaries, releasing trapped gases of VOCs and exposing new surfaces. Because of the poor retentive properties of soils in general for VOCs (Chiou, 1989), and these two release mechanisms (disaggregation and exposure), sample collection and handling should be performed with limited disruption and exposure (T.M. Spittler, personal communication; Lewis et al., 1991).

SUMMARY

The following general outline should be incorporated into site sampling protocols if soils are to be collected for VOC analysis:

- Soil samples should be retrieved from freshly exposed surfaces.
- Transfers should be made with a coring device with an o.d. which fits into the i.d. of the sample container.
- Soil subsamples should be put only into vials that:
 - are three quarters full of Type 1 water (for HS/GC analysis);
 - contain a sufficient amount of MeOH (for high level "> lug/g" PT/GC/MS analysis);
 - are equipped with a purge-and-trap vial adapter (for low level "< 1 ug/g" PT/GC/ MS analysis).
- Soiling of the threads and sealing surface of the collection vial should be avoided.

NOTE: Although not covered in this study, preservatives often will be necessary to limit biodegradation of aerobically labile VOCs.

The advantages of using this sampling protocol are:

- VOC losses are minimized by minimizing soil surface area exposure.
- Sampling time efficiency is maximized.
- 3. Closure leakage is eliminated.
- The volume of contaminated soil that leaves the site for chemical analysis is minimized.
- Aqueous extraction HS/GC in a screening application:
 - can be performed with the objective to reduce the number of background (blank) analyses performed by PT/GC/MS;
 - can meet data quality objectives set during various phases of a site investigation, allowing samples to be processed on site, decreasing the turn-around time and overall analytical costs;
 - provide an initial assessment allowing the contract laboratory to establish which sample (one extracted with MeOH or designed to be purged directly) should be analyzed by PT/GC/MS.

CONCLUSION

Disruptive soil collection and handling protocols are prone to losing greater than 95% of the VOC retained by native sandy-silt vadose zone soils. Intergranular disruption, unnecessary exposure, and soiled closure surfaces all contribute to the losses of VOCs that are weakly bound to soil particle mineral surfaces or transiently exist among the soil voids.

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REVIEW OF RECENT FINDINGS IN WELL-CASING STUDIES

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ABSTRACT

For some time regulatory agencies have been concerned about 1) whether casing and screen materials used in groundwater-monitoring sorb or leach analytes of interest and 2) the resistance of these materials to degradation by the environment. This paper reviews recent findings on the suitability of several types of well casings for groundwater-monitoring applications.

INTRODUCTION

In 1986, The EPA's Resource Conservation and Recovery Act (RCRA) Ground-Water Monitoring Technical Enforcement Guidance Document (or the TEGD) (USA EPA, 1986) stipulated that fluorocarbon resins or stainless steel should be used for all well casings and screens in the saturated zone when monitoring for volatile organics. The use of polyvinylchloride (PVC) casings and screens was not allowed because they might sorb or leach contaminants, thereby affecting the integrity of samples, and because they could not withstand exposure to some solvents. This paper addresses these issues and looks at the general suitability of stainless steel, PVC, and polytetrafluoroethylene (PTFE) well casings for groundwater monitoring.

EFFECTS OF WELL CASINGS ON SAMPLE INTEGRITY

Leaching and Sorption of Metals by Casings

Previous studies by our laboratory (Hewitt 1989, 1992; Parker et al. 1990), have compared the ability of four well-casing materials (PVC, PTFE, stainless steel 304 [SS 304] and stainless steel 316 [SS 316]) to sorb organics and metals and leach metals. With respect to leaching and sorption of metals by these materials, these studies revealed that PTFE was clearly the best and stainless steel casings were the worst.

Hewitt (1989) looked for leaching of As, Ag, Cd,

Cu, Cr, Pb, Se, and Hg from these four materials. PTFE did not leach any of these metals at statistically significant levels when compared with controls that contained no casings. In contrast, after 1 day, PVC leached significant levels of Cr and Pb, SS 316 leached significant levels of Cr, Cd, and Pb, and SS 304 leached significant quantities of Cr and Pb. With the exception of initial concentrations of Pb, leached concentrations were always higher for the two stainless steel casings than for PVC (Figures 1, 2, 3). The concentrations of Cr, Cu, and Pb tended to increase with time in samples exposed to the stainless steel casings (Figures 1, 2, 3), showing that continued release of these analytes can be expected; this was not the case for PVC (Figure 3). I would expect that corrosion of stainless steel casings and screens would greatly enhance this problem over the long term. On the other hand, it appears that leaching of Pb and Cr from PVC is a surface phenomenon. Packham (1971) found that the leaching of lead stabilizers from PVC pipe was a surface phenomenon and that leachates could be reduced substantially by pretreatment with either alcoholic sodium hydroxide or a mixture of dilute nitric and perchloric acids. High variability was seen in the data for samples exposed to the stainless steel casings and was initially attributed to oxidation that occurred in many of the samples during the course of this study. As a follow-up, a similar study was conducted under less corrosive conditions (lower dissolved oxygen or D.O.) and produced similar results, although there was no observable oxidation in these samples (Hewitt 1992). In this study, significant levels of Fe, Ni, Cd, and Cu were leached from the stainless steel casings after only 2 hours.

Parker et al. (1990) looked for sorption of several metals (As, Cr, Pb, and Cd) by the same four materials. They found that, except for slow loss of Pb, PTFE casings had no significant effect on the concentration of these metals (Table 1). For the other casings, changes in

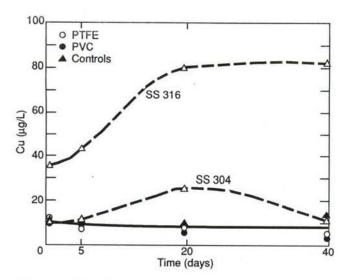


Figure 1. The effects of well casings on Cu concentrations (from Hewitt 1989).

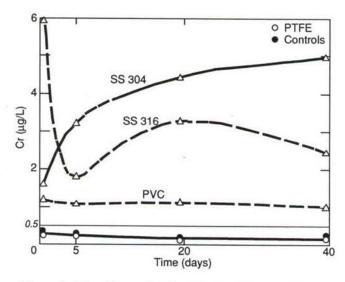


Figure 2. The effects of well casings on Cr concentrations (from Hewitt 1989).

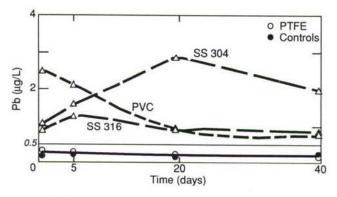


Figure 3. The effects of well casings on Pb concentrations (from Hewitt 1989).



Table 1. Time for 10% Change in Metal Concentrations (from Parker et al. 1990).*

	-		Lo	SS			Ga	in
	A	S	C	r	P	b	(Cd
PVC	> 72		> 72		4	(10%)	4	(13%)
PTFE	> 72		> 72		72	,	> 72	(2010)
SS 304	24	(12%)	> 72		4	(22%)	4	(17%)
SS 316	24	(15%)	8	(23%)	4	(20%)	4	(24%)

^{*} Sample times: 0.5, 4, 8, 24, and 72 hr. Values in parentheses are the actual amount lost.

concentrations often exceeded 10% in 8 hours or less and thus could bias analyses of samples taken from wells constructed with these materials. Specifically, PVC casings sorbed Pb and leached Cd, SS 316 casings sorbed As and Pb and leached Cd, and SS 304 casings sorbed As, Cr, and Pb and leached Cd. Both stainless steel casings showed markedly poorer performance than the PVC casings. Again there was high variabilty in the data for samples exposed to the stainless steel casings. Results were very similar under less corrosive (low D.O.) conditions (Hewitt 1992).

Sorption and Leaching of Organics by Casings

In contrast with the results found for sorption and leaching of metals, Parker et al. (1990) found that stainless steel was the most inert with respect to sorption of organics while PTFE was the most sorptive. In this study, the same four materials were exposed to a mixed solution (2 ppm) of 10 organics under sterile conditions. The organics tested were hexahydro-1,3,5-trinitro-1,3,5triazine (RDX), 1,3,5-trinitrobenzene (TNB), cis- and trans-1,2-dichloroethylene (CDCE and TDCE), mnitrotoluene (MNT), trichloroethylene (TCE), chlorobenzene (CLB), and o-, p-, and m-dichlorobenzene (ODCB, PDCB, and MDCB). These compounds were selected based on their molecular structure, solubility in water, octanol-water partition coefficient (Kow value), and retention time (using reversed-phase HPLC).

The results for TCE, given in Figure 4, are typical for all the organics where losses were observed. There

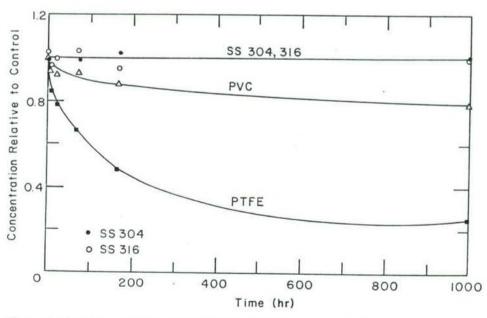


Figure 4. Sorption of TCE by SS 304, SS 316, PVC, and PTFE well casings (from Parker et al. 1990).

Table 2. Time for 10% Loss of Selected Organics (from Parker et al. 1990).*

Compound	PTFE	PVC
RDX	> 6 wk	> 6 wk
TNB	> 6 wk	> 6 wk
CDCE	6 wk (20%)	6 wk (20%)
TDCE	24 hr	1 wk
MNT	1 wk	< 6 wk
TCE	8 hr	6 wk
CLB	24 hr	6 wk
ODCB	24 hr	6 wk
PDCB	8 hr	1 wk
MDCB	8 hr	1 wk

^{*} Sample times: 0, 1, 8, 24, 72 hours, 7 days, and 6 weeks.

is no loss of TCE in samples exposed to either stainless steel casing, even after 6 weeks; the rate and extent of loss was greatest for PTFE. There is some slow loss with PVC, but the rate and extent of sorption is much less than with PTFE. Not all compounds were sorbed at measurable levels by PTFE; those that did include CDCE, TDCE, CLB, ODCB, MDCB, and PDCB. For PTFE, it took 8 to 24 hours to see a 10% loss of these compounds, while it took 1 to 6 weeks to see an

equivalent loss in samples exposed to PVC (Table 2). MDCB and PDCB were sorbed to the greatest extent, 74% loss after 6 weeks. Two analytes, RDX and TNB, were not sorbed at measurable levels by any of the casings, even after 6 weeks.

We were able to correlate the loss of hydrophobic organic constituents in the solutions exposed to PTFE casings with the substance's K_{ow} value (Figure 5). The greater the K_{ow} , or the more hydrophobic the substance,

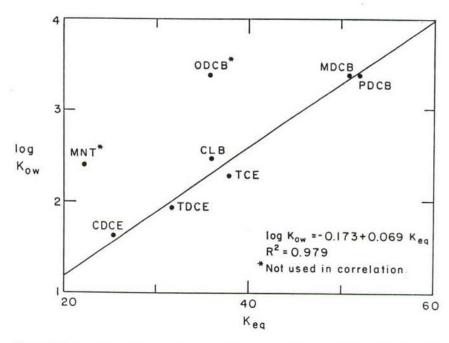


Figure 5. Correlation between log octanol-water partition coefficient (K_{ow}) and log equilibrium constant (K_{eq}) for organic solutes exposed to PTFE casings (from Parker et al., 1990).



Table 3. Time (hours) for Concentration to Be Significantly Different from 1.0 (from Gillham and O'Hannesin 1990).*

	Benzene	Toluene	Ethyl- benzene	m-xylene	o-xylene	p-xylene
SS	> 1344	> 1344	> 1344	> 1344	> 1344	> 1344
PVC (rigid)	48-96	24-48	12-24	12-24	12-24	12-24
PTFE	24-48	3-6	1-3	3-6	6-12	1-3
PVC (flexible)	0-01	0.1	0-0.1	0-0.1	0-0.1	0-0.1

^{*} Approximately a 10% loss.

1344 hr = 56 days

the greater the tendency to be sorbed by PTFE. However, this correlation overestimates losses for more polar organics. While it is difficult to extrapolate this test data to a sampling situation, we felt the rate of loss of several organics when exposed to PTFE was rapid enough to impact concentrations of some compounds in some circumstances.

This study agrees well with a similar study conducted by Gillham and O'Hannesin (1990) that looked for sorption of several aromatic hydrocarbons (ppm levels) by several materials used in sampling groundwater (stainless steel, rigid PVC, and PTFE) under sterile conditions (Table 3). Our study also agrees reasonably well with a study by Reynolds and Gillham (1986) that examined losses of ppb-level halogenated alkanes and alkenes. Although losses were not always greater for PTFE than for PVC in this study (Table 4), biological activity cannot be ruled out. However, the most significant finding of this study is the very rapid sorption of tetrachloroethylene by PTFE; the loss was

10% within 5 minutes. Another study by Reynolds et al. (1990) found that stainless steel was not inert in all cases. They observed substantial losses of two of five halogenated compounds (bromoform and hexachloroethane) in solutions exposed to stainless steel (Table 5). These two compounds were the most highly halogenated of the group, and the loss of these compounds occured rapidly after a 2-week lag. The authors attributed this loss to reductive hydrogenolysis as a result of leaching of transition metal ions (such as Cr, Mn, Fe, and Ni) from the stainless steel. Based on our findings from our inorganic leaching studies (Hewitt 1989, 1992), this explanation is entirely plausible, although losses due to biological activity cannot be ruled out.

In several of the previous studies (Parker et al. 1990, Gillham and O'Hannesin 1990, Reynolds and Gillham 1986), losses were attributed to absorption within the polymer matrix rather than adsorption by the surface. If losses were due to adsorption, then the extent of this loss would depend upon the number of available

Table 4. Time for a 10% Loss of Organics (from Reynolds and Gillham 1985).

	1,1,1– trichloroethane	Tetrachloro- ethane	Bromoform	Hexachloro- ethane	Tetrachloro- ethylene
PTFE	~ 1 day	~ 2 wk	> 5 wk	~ 1 day	< 5 min
PVC	~ 5 wk	~ 2 wk	~ 3 days	~ 1 day	~ 1 day

Table 5. Time (days) for 50% Loss of Organics (from Reynolds et al. 1990).

	1,1,1– trichloroethane	Tetrachloro- ethane	Bromoform	Hexachloro- ethane	Tetrachloro- ethylene
SS	> 35	> 35	31	32	> 35

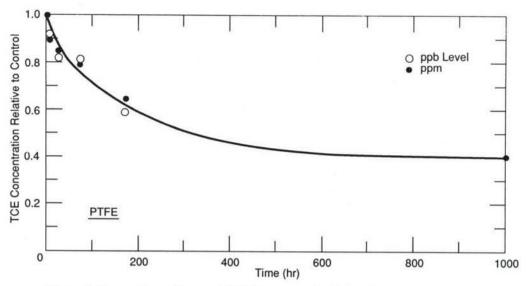


Figure 6. Comparison of losses of TCE in ppm and ppb solutions exposed to PTFE.

sites, and one would predict that the percent loss would be greater at lower concentrations. Figure 6 compares sorption of a 2-ppm solution of TCE by PTFE (Parker et al. 1990) with recent results for a 20-ppb solution. The percent losses are equivalent. This was also true for PVC as well as for all of the other compounds tested to date (RDX, TNB, MNT, TDCE, and CDCE). Thus, we can conclude that for PTFE and PVC organics are absorbed within the polymer matrix. Once again there were no losses observed in any of the samples exposed to stainless steel casings under sterile conditions.

With respect to leaching of organics from rigid PVC, several studies are available in the literature. While plasticizers are often found to leach from flexible PVC, this is not the case for rigid PVC. This is because the plasticizer content of flexible PVC ranges from 30–50% by weight (Junk et al. 1974 Aller et al. 1989) while rigid PVC contains virtually no plasticizers (<0.01%) (Barcelona et al. 1984) and thus would not be expected to leach large quantities of plasticizers.

Curran and Tomson (1983) compared the leachates from PTFE (Teflon), flexible PVC (Tygon tubing), and rigid PVC. Using gas chromatography following preconcentration on an XAD-2 column and solvent extraction, they found the least amount of contamination was leached from PTFE and that rigid PVC was a very close second. In contrast, they found large quantities of contaminants leached from flexible PVC.

Miller (1982) also was unable to find any organic constituents leached from rigid PVC using flame ionization-gas chromatography following solvent extraction and a thousandfold concentration.

PVC pipe has also been found to leach alkyl tin compounds (stabilizers) (Boettner et al. 1982) and vinyl chloride monomer, although standards set for well casings by the National Sanitation Foundation in 1977 have substantially reduced leached conentrations of vinyl chloride monomer to 1–2 ppb (Barcelona et al. 1984, Aller et al. 1989).

RESISTANCE OF MATERIALS TO DEGRADATION BY THE ENVIRONMENT

The conditions that cause the corrosion of stainless steel are well documented in the literature. These include low pH, high dissolved oxygen content, presence of hydrogen sulfide, high dissolved solids, high carbon dioxide, high chlorides, and the presence of either sulfate-reducing bacteria or bacteria that utilize hydrogen (Aller et al. 1989, Driscoll 1986). While it is also commonly known that several neat solvents can degrade PVC, the effect of high aqueous concentrations of these solvents on the structural integrity of PVC is not generally known. Among the solvents known to degrade rigid PVC are low molecular weight ketones, aldehydes, amines, and chlorinated alkanes and alkenes (Barcelona et al. 1984).

Berens (1985) noted that the solvent interaction parameter (χ) used in the Flory-Huggins equation could be used as a measure of the solvent or swelling power of a particular solvent for rigid PVC. Table 6 gives the χ values for a number of organic solvents for PVC. In general, PVC is only softened by solvents with a χ value less than 1; the lower the number, the greater the

Table 6. Polymer-Solvent Interaction Parameters (x) for a Series of Organics (from Berens 1985).

Compound	X
Methylene chloride	< 0.53
Trichloromethane	9.64
1,1-dichloroethane	< 0.68
1,1,1-trichloroethane	0.85
Trichloroethylene	0.88
Tetrachloroethylene	1.17
Benzene	0.68
Toluene	0.83
Acetone	0.61

solvent/swelling power. A solvent with a χ value less than 0.5 can completely dissolve the polymer.

Berens predicted the permeation of organics through PVC pipe based on samples of PVC exposed to a range of concentrations (activities) of these solvents. He found that the rate of penetration into PVC changed many orders of magnitude as the activity of the penetrant changed. At ambient temperatures, rigid PVC would only be softened by strong solvents or swelling agents of PVC (with $\chi=0$) at activities > 0.5. For less aggressive solvents, even higher activities would be needed. Figure 7 shows the isotherms Berens derived using the Flory-Huggins equation for various values of χ and the approximate softening range for PVC. For example, for a compound with a $\chi=0.5$, softening should occur in solutions with activities greater than 0.6.

For aqueous solutions, the solvent activity can be approximated by dividing the concentration of the compound in solution by its solubility in water. Thus, for aqueous solutions of solvents to cause softening of rigid

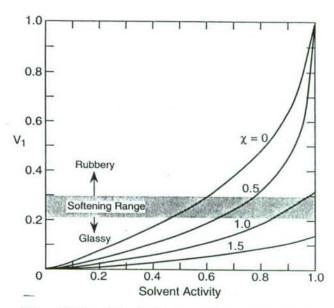


Figure 7. Flory-Huggins isotherms for different values of χ and the approximate softening range for PVC (from Berens 1985).

PVC, the solvent must be able to dissolve PVC and must be present in the water at a concentration that exceeds one-half its aqueous solubility. Berens therefore concluded that softening of PVC is only possible in the presence of nearly undiluted solvents or swelling agents of PVC.

One criticism of Berens' work is that he tested different activity solutions by dissolving the solvents in polyethylene glycol but never actually tested aqueous solutions of these solvents. We have conducted two preliminary studies addressing this issue.

In the first study, we exposed pieces of PVC, PTFE, SS 304, and SS 316 to aqueous solutions of a

Table 7. Times for Softening of PVC in Solutions at Various Activities (from Parker et al. 1992).

Activity	Time to Pronounced Softening*	Time to Slight Softening
1.0	4 days	←
0.8	22 days	4 days
0.6	> 33 days	15 days
0.4	> 33 days	33 days
0.2	> 33 days	> 33 days
0.0	> 33 days	< 33 days

^{*} Sample could be bent back on itself.

mixture of toluene, tetrachloroethylene, o-dichlorobenzene, and p-dichlorobenzene (Taylor and Parker 1990). Each compound was at concentrations 0.25 times its respective solubility in water (approximate activity = 0.25). The casings were soaked in these solutions for up to 6 months and then examined for changes in surface structure using the scanning electron microscope (SEM). No changes in surface structure were noted even in the PVC pieces that had been exposed for 6 months.

In the second study, small pieces of PVC well casing were exposed to aqueous solutions of methylene chloride at approximate activities of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 (Parker et al. 1992). The samples were monitored for changes in weight gain, length, flexibility, and curvature. We also looked for any changes in surface structure using the SEM. The study ran for 33 days. The results agree reasonably well with Berens' predictions. Samples exposed to the highest activity solution (1.0) softened within the first 4 days, and samples exposed to the 0.8 activity solution were softened after 22 days (Table 6). As predicted, samples exposed to the lowest activity solution (0.2) showed no signs of softening. However, samples exposed to the 0.4 and 0.6 activity solutions showed some slight changes, indicating softening might occur eventually, especially at the 0.6 activity. Berens would predict that softening would occur in solutions at a 0.6 activity if the χ value of methylene chloride is around 0.3. He estimated that this value was less than 0.53 but did not give an actual number. Further longer-term studies will be conducted shortly to clarify this issue. Conservatively, however, we can say that there should be no softening of rigid PVC in solutions of methylene chloride at activities below 0.2. This corresponds to a very high concentration of methylene chloride: 3340 mg/L. In most environmental situations, therefore, aqueous solutions of methylene chloride, or any other solvent, will not cause serious swelling or softening of PVC pipe.

For a more thorough review of the literature on these subjects, please see Parker [in press].

CONCLUSIONS

From these studies we can conclude that neither SS 304, SS 316, PTFE, or PVC can be used in all circumstances. Stainless steel and PVC casings can leach significant quantities of some metals. The amount of leaching was generally much greater for samples exposed to stainless steel casings than for PVC, and levels continue to increase in samples exposed to stainless steel even if there is no visible sign of corrosion. In contrast, stainless steel is the most inert with respect to sorption, or loss, of organics. PVC and PTFE will absorb organics within their polymer matrix. For PTFE, the rate and extent of absorption depends on the hydro-

phobicity of the organic. The more hydrophobic the substance, the greater the tendency to be sorbed by PTFE. The concentration of these organics will not affect the percent of sorption for either PVC or PTFE. Thus, in most groundwater monitoring situations, PVC appears to be the best compromise material. However, it should not be used if one expects to encounter neat PVC solvent or very high concentrations (exceeding 0.2-0.5 times solubility) of these solvents, and stainless steel should not be placed in a corrosive environment.

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Evaluating the Effectiveness of Interim Remedial Actions at Source Areas D and G

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Evaluating the Effectiveness of Interim Remedial Actions at Source Areas D and G

Twin Cities Army Ammunition Plant Minnesota

Introduction

This paper is a case study of the large-scale remediation of soil and groundwater contamination at the Twin Cities Army Ammunition Plant in Minnesota. These award-winning interim remedial actions were the first and largest step toward the cleanup of multiple source areas. Work at two of the most critical source areas demonstrated techniques that:

- Provided a fast and technically feasible response and implementation under extreme political and regulatory pressure
- Substantially reduced costs using effective technology
- Prioritized the removal of the source of contamination, with dramatic cost/removal advantages over groundwater containment

The Plant

The Twin Cities Army Ammunition Plant (TCAAP) in New Brighton,

Minnesota, is owned by the U.S. Army and operated by Federal Cartridge

Company (FCC) (Figure 1).

When completed during World War II, the 2,300-acre site contained 323 buildings, including seven major production facilities.

From 1941 to 1976, except for temporary shutdowns, TCAAP manufactured and tested small arms ammunition and related materials, and handled and stored strategic and critical materials for other government agencies.

TCAAP is now on standby status.

Several other private companies conduct operations on the facility as tenants. Two major long-term lessees are Honeywell and 3M. Honeywell has manufactured ammunition and fuses, and 3M has manufactured self-luminous materials, medical products, and static eliminators.

Today TCAAP is primarily surrounded by residential neighborhoods, with some commercial property. Another concern regarding the setting is that the site is underlain by sandy soils and bedrock that is highly fractured and irregularly eroded--conditions that facilitate the spread of contamination.

Investigation and Negotiations

In 1978, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) issued a report on waste disposal activities and the uses of potentially toxic or hazardous chemicals and radioactive materials at TCAAP. Following this report were investigations by various parties which identified 14 potential source areas that had been burial or open-burning areas, or industrial sources of contamination.

In 1981 the Minnesota Pollution Control Agency (MPCA) and later the Minnesota Department of Health identified volatile organic compounds in wells on-site and in three communities. Based on EPA criteria, contaminant levels were chronically toxic in most of the wells and acutely toxic in several others.

Investigations showed that the plume of contaminated groundwater migrated at least three miles off-site. The next year TCAAP and the New Brighton/Arden Hills area were put on the National Priorities List for Superfund cleanup with a hazard ranking of 59.

Extensive communications began in the 1980s among the EPA, MPCA, Army, FCC, and Honeywell. In 1987, the EPA, MPCA, and Army entered into the nation's first Federal Facility Agreement for investigation and cleanup.

While negotiations continued, interim remedial actions were taken to control the more severe contamination. The Army assisted the EPA and MPCA in emergency actions to modify water supplies in two communities and supply municipal water or bottled water for residences with private wells.

Next, the Army announced its plan to take interim remedial actions at TCAAP in June 1985. These actions involved the two most critical source areas (Figure 2). At Source Area D, several pits had been used for two decades for the burning or disposal of wastes such as solvents, oil, powder, rags, neutralized cyanide, and scrap explosives. For three decades, Source Area G had been a general disposal area for barrels, rubble, asphalt, and other wastes. Both areas were heavily contaminated by solvents (volatile organic compounds) such as trichloroethene (TCE). Source Area D was also contaminated with polychlorinated biphenyls (PCBs).

The interim remedial actions at Source Areas D and G consisted of two major projects: solvent remediation using in-situ volatilization at both sites, and PCB remediation using thermal treatment at Source Area D.

The remedial investigation began in May 1987 and was completed in November 1991. The feasibility study is scheduled for completion in 1994.

Solvent Remediation: Planning

In-situ volatilization (ISV) uses air stripping technology to remove solvents from soil without excavation. Vents (slotted pipes) are installed in the soil and a blower draws air through the vents to cause volatile organic compounds (VOCs) to volatilize into the air stream. At the surface the VOCs in the exhaust are dispersed directly into the air or through carbon contactors.

ISV was considered a sound alternative for TCAAP because of its costeffectiveness and because it reduced potential for human contact with the
contaminants. This interim action was not intended to resolve deeper
contamination but to remove solvents from the shallower soil, which was the
primary source of contamination. By removing contaminants, ISV prevents
additional groundwater contamination, which costs more per pound of contaminant
to remediate.

To evaluate the effectiveness of this relatively new technique at TCAAP, USATHAMA performed a 14-week pilot study (November 1984 through February 1985). The results showed great promise, with removal of TCE concentrations as high as 350 ppm. It is estimated that the test alone removed approximately half a ton of VOCs.

In order to begin cleanup as quickly as possible, Wenck was asked to design the full-scale system without conducting further studies. This was a challenge due to the limited experimental data, yet the system was designed in three weeks. In addition, Wenck selected standard equipment and materials that were readily available for construction.

The design required flexibility and margins of safety because the full-scale systems required much higher flow rates than were used in the pilot study, and the conditions at Source Area G could differ from those at Source Area D, where the pilot study occurred.

For example, valves and sampling ports were placed at strategic locations so that any vent or combination of vents can be monitored and isolated. As a result, one can identify areas with different levels of contamination than expected and add vents or adjust flow rates as needed.

Another design consideration was the Minnesota climate. Although PVC was used for the soil vents, steel was selected for the more vulnerable aboveground piping because it is more durable and less prone to brittleness after extended exposure to the cold. The aboveground system was insulated, heat-taped, and supported on wooden cradles to prevent ice buildup in the piping interior.

Solvent Remediation: Implementation

Before the ISV systems were built, Source Areas D and G were capped with 18 inches of clay to avoid further leaching of contaminants by precipitation.

Before capping Source Area D, the PCB-contaminated soils were excavated for later remediation.

The entire ISV system installation was completed within two months--a full six months before it was thought possible by government agencies.

Construction began in November 1985 and, despite winter conditions, was completed by year's end.

The TCAAP systems have a total of 129 vents. At Source Area D, the grid covers an area of approximately 130 feet by 200 feet, and at Source Area G the grid covers an area of approximately 190 feet by 360 feet. The subsurface setting at both areas is highly variable, so vent spacings of 25 feet were selected to ensure effective cleanup. (See Photo 1.)

The vents are 35 to 55 feet deep in the unsaturated zone, where the majority of contamination was present. An additional vent was installed to capture VOCs at the 125- to 150-foot depth. The vents are 3-inch diameter slotted PVC surrounded by gravel pack to protect the vents from clogging. The top of each vent is grouted to ensure a reasonable seal. The vents connect to steel lateral pipes 8 inches in diameter which lead to 18- and 24-inch diameter steel header pipes. (See Figure 3.) Each of the two ISV system has four blowers contained in a prefabricated building along with electrical controls.

Over 1,200 pounds of VOCs were removed the first day of operation at Source Area D, with 20,000 pounds of total VOCs removed in the first 37 days. At the larger Source Area G, 4,600 pounds of total VOCs were removed the first day, with 24,000 pounds of total VOCs removed in the first 14 days.

Because of this phenomenal success, the systems were shut down so that air emissions could be evaluated. Air quality modeling and studies were performed and discussions were undertaken with the Minnesota Pollution Control Agency and the EPA.

That summer, Source Area D resumed operation at lower flow rates, and Source Area G resumed operation after 8,000-pound granular activated carbon units were added to the air exhausts. The carbon was removed and shipped to an off-site facility for reactivation.

A thorough air monitoring program has been used since the start of operation and monitoring has revealed no air quality deterioration. As a result, the MPCA later approved removal of the carbon units at Source Area G.

Solvent Remediation: Results

Since 1986 the ISV systems have removed over 100 tons of solvent and are considered among the largest in the country relative to the amount of solvent recovered. In addition, contaminant levels in the groundwater plume have significantly decreased due to these interim measures.

Figures 4 and 5 show VOC removal rates for each area. They show a corresponding decrease in VOC removal as VOC levels in soil decrease over time.

Because the soils do not have to be excavated, ISV reduces the potential for human contact and has low capital and operating costs, especially when the carbon is regenerated. For the same reason, ISV is attractive in states like Minnesota that no longer allow the land disposal of large volumes of contaminated soil.

Operating costs are relatively inexpensive if the ISV system can be "throttled back" to maintain emission rates within regulatory requirements and operated with no emission controls. Labor and electrical costs are very low, with the only major item being sampling and analysis to verify the amount of VOC removal. Even with the use of emission controls, operating costs can be reduced if the carbon is regenerated.

This project demonstrates dramatic differences between removal of the source or mass of contamination versus groundwater pumpout for plume containment and/or water treatment.

Tables 1 and a compare the cost and effectiveness of these two approaches.

As shown in Table 1, ISV at Source Areas D and G alone removed nearly three times the amount of the contaminants that were removed from groundwater at the other sites.

As shown in Table 2, annual operating and maintenance costs are dramatically lower for ISV than for groundwater measures. Construction cost more for Source Area G because of the addition of GAC units. However, even this cost is far below the cost of groundwater pumpout followed by air stripping.

In addition to weighty advantages in effectiveness and cost, ISV is extremely easy to implement. Construction of the relatively simple ISV system can be completed in a matter of weeks, with little maintenance or "fine-tuning." Because ISV attacks the problem at its source, ISV achieves a longer-term solution than gradient control or even groundwater treatment.

In conclusion, ISV has multiple advantages over groundwater containment and even groundwater treatment, especially as an interim remedial action that must produce big results fast. The ISV systems removed large amounts of solvent over a short timeframe, thereby providing greater protection of human health and the environment more quickly.

The solvent remediation project earned a Grand Award for outstanding achievement from the Consulting Engineers Council of Minnesota and received recognition from the American Consulting Engineers Council.

PCB Remediation: Planning

PCB contamination in soils at Source Area D ranged up to 210 parts per million (ppm), with an average of 71 ppm. This high level of contamination and the unknown extent of PCB migration required immediate action. TCAAP's goal for the PCB contamination was clean closure, and the Toxic Substances Control Act required 99.9999 percent destruction of PCBs.

To begin, 1,400 cubic yards of PCB-contaminated soil were excavated at Source Area D. The soils were stored on a 40-mil high-density polyethylene (HDPE) liner with a 20-mil cover. The HDPE sheets were welded together to create a sealed envelope. The storage area covered a 100-foot by 100-foot area. The excavation was performed immediately before the ISV system was installed at Source Area D in 1985.

Once the PCB-contaminated soils were temporarily secured, FCC performed a feasibility study on alternative remedial actions and identified on-site thermal treatment as the preferred alternative. Twice during 1987, soils from Source Area D were successfully tested on-site using the Shirco Infrared Systems Portable Test Unit. The tests showed 99.9999 percent destruction of the PCBs. This level of destruction was required by the Toxic Substances Control Act. The pilot testing also showed adequate destruction of other organic compounds and metals.

After these tests, Wenck prepared the interim remedial action plan for PCBs, which was approved in 1989 by the MPCA and EPA Region V. Later activities included a 30-day public comment period, a public meeting, and two risk assessments by FCC and the EPA. State and federal permits were obtained.

PCB Remediation: Implementation

Beginning in the summer of 1989, the area for thermal treatment was graded and concrete pads were installed for feed preparation, equipment, and ash storage. The first two pads had 16-inch high cinder block walls to contain contaminated runoff. The ash storage pad had 48-inch high walls and four partitioned storage areas. Facilities were installed so that process water and runoff could be treated and then discharged to the sanitary sewer. Other installations included electricity, propane, water, and private sanitary sewer.

A full-scale mobile incinerator was brought on-site via 18 tractor trailers.

After installation, a shelter was constructed to protect the equipment from unnecessary temperature loss by precipitation.

Before opening the sealed stockpile, five PVC vent screens were installed to release airborne volatile organic compounds to the existing ISV system. Then the liner was opened and soils were removed using a backhoe and hand tools.

Pumps were on-hand to collect accumulated precipitation at the open stockpile for on-site treatment.

The soils were taken to the feed preparation pad for crushing and screening to produce material less than 1 inch in diameter. In addition, cost-efficient No. 4 fuel oil was mixed with the soil to increase the soil's BTU value for PCB volatilization.

Once the soils were prepared, they were placed via front-end loader into a hopper and conveyor belts fed the soils to the primary chamber. The belt outside the chamber was enclosed to prevent fugitive dust emissions. A mechanical cakebreaker ensured that the soils were uniformly exposed to treatment.

The soils were exposed to a maximum temperature of 1,450° Fahrenheit and then discharged. The heat was generated electrically by ceramic heating rods.

The secondary combustion chamber thermally treated the vaporized organic compounds from the primary chamber at 1,950-2,000° F. Emissions then passed into a wet scrubber where the gases were neutralized and particulates were removed prior to discharge to the atmosphere through a stack.

Blowdown water was treated in a clarifier and, when necessary, filtered to remove solids, prior to discharge to the municipal sanitary sewer system.

After the project was completed, the equipment, water basin liners, concrete pads, and other materials were decontaminated and the operation was dismantled.

The treated soil was temporarily stockpiled until it was analyzed to ensure compliance with the required treatment level and later placed on-site, graded, covered with topsoil, and vegetated.

PCB Remediation: Sampling and Monitoring

Soil samples were collected before construction of the treatment facility to confirm that no contamination remained at the site. Monitoring at the ISV system ensured that the exhausted VOCs from the sealed stockpile were within the permitted limits. During removal of the contaminated stockpile, the liner was rolled back to sample the underlying soils to ensure that no contamination had been released.

Treated soil from the discharge conveyor was sampled hourly for the first eight hours of treatment and then composited. Afterwards, hourly samples were collected during the 12 hours required to fill a storage bin and were composited once the bin was filled. The composites were analyzed for PCBs with a 24-hour turnaround so that operational changes could be made quickly, if necessary. Soils

with PCB concentrations over 2 ppm were to be returned for re-treatment. A composite sample was also analyzed for EP-toxic metals.

During incineration, the site was constantly monitored for spills and leaks, the emergency annunciator was tested daily, and operations were continuously checked for safety and efficiency. Level C protection was used, which included a full-face respirator.

During incineration, an organic vapor analyzer was used to monitor ambient air quality three times a day at eight stations. As required under TSCA, emissions from the secondary combustion chamber were monitored for oxygen, carbon monoxide, and carbon dioxide using continuous recorders.

Treated process water and runoff were also monitored with 24-hour laboratory turnaround and the results were sent by facsimile to the Metropolitan Wastewater Control Commission for approval before discharge to the municipal sanitary sewer. All discharges were approved.

PCB Remediation: Results

The project successfully destroyed the required 99.9999 percent PCBs.

Total on-site destruction of the PCBs eliminated the need to transport and dispose of the contaminated soils at a hazardous waste landfill. This eliminated the potential for public contact, the long-term liability of landfilling, and the need to provide financial assurance.

Instead of disposing of 1,400 cubic yards of contaminated soil and other residuals, only 53 55-gallon drums required disposal. These drums contained materials that could not be incinerated on-site and were transported to an Arkansas hazardous waste facility for disposal or incineration. The material included metal debris, rock, residual soil, contaminated wood, steel and concrete dust, Tyveks protective clothing, the liquid storage liners, and water treatment sludge.

Infrared treatment was relatively new at the time and the TCAAP project was the first time infrared had been used for PCBs at a federal facility.

Because infrared relies on electricity instead of combustion, it has fewer emissions. This advantage is especially important regarding PCBs because of the potential for dioxin or hydrochloric acid emissions. Ambient air at the TCAAP project was never found to exceed background levels and stack emissions were satisfactory.

With continuous operation at 100 tons per day, the incineration was completed in six weeks instead of the original 13-week schedule. The PCB cleanup cost \$1.4 million.

The design team received an award from the Consulting Engineers Council of Minnesota for the phenomenal success of the PCB remediation.

Overall Environmental Monitoring

Besides the activity at Source Areas D and G, several other remedial actions have taken place at other source areas. Long-term ongoing monitoring is critical to characterize overall environmental conditions and cleanup performance. TCAAP's monitoring program involves the plant and surrounding areas with more than 300 groundwater monitoring wells.

This large-scale monitoring system requires a substantial budgeting commitment. For example, the capital cost was approximately \$4.3 million, with total annual costs approaching \$0.5 million.

Adjustments in the monitoring plan are made as needed. For example, it was found that changes in the overall plume are slow from year to year and that annual monitoring is adequate. The data also indicate a possible separate source of contamination unrelated to the army ammunition plant. This finding is important to protect TCAAP from unwarranted environmental liability and cost.

We are just now beginning to see results of the interim remedial actions taken in mid-1980s, and the full results regarding cleanup levels and closure achievements won't be realized for years. However, information to date clearly indicate that the PCB removal and ISV systems at Source Areas D and G have made significant decreases in groundwater contamination.

Summary

TCAAP is a dramatic demonstration of the cost-effectiveness of in-situ volatilization, especially in comparison with groundwater containment and groundwater treatment after pumpout. Infrared thermal treatment of PCBs also proved to be a cost-effective alternative for contaminated soils. The combined efforts of the design team resulted in profound reductions in soil contamination which in turn greatly reduced the threat to public health and the environment.

TABLE 1

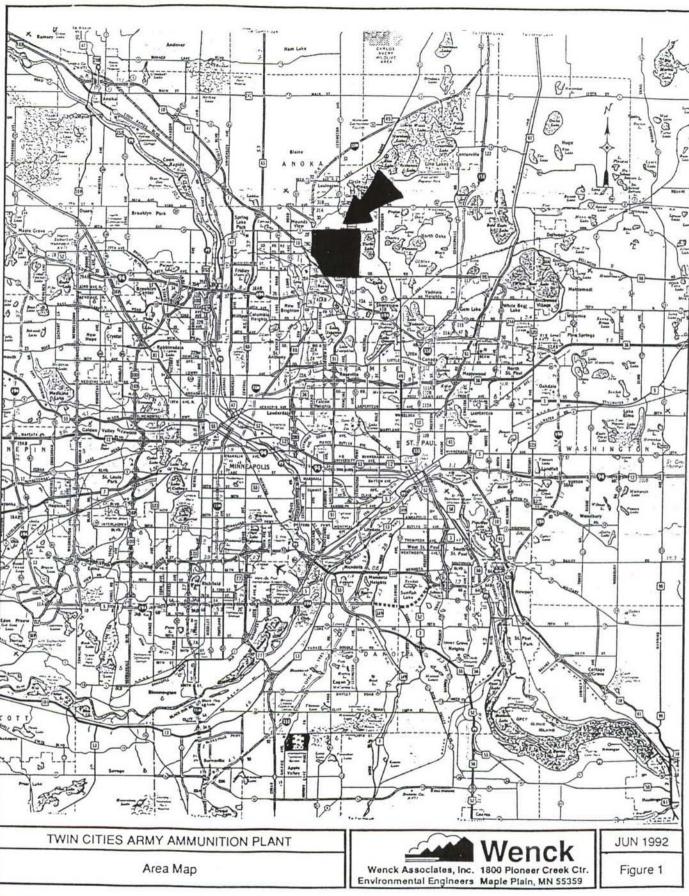
Comparison of Mass Removal by ISV and Groundwater Measures Twin Cities Army Ammunition Plant (March 1992)

Site	Treatment Technology	Year Started	Solvent Removed
Source Area A (Disposal and Open-burning Pits Similar to Source Areas D and G)	One Pumpout Well with Granular Activated Carbon Treatment	1988	3 Pounds
Source Area I (Building with Spills and Sewer Disposal)	One Pumpout Well with Air Stripping Treatment	1987	305 Pounds
Source Area K (Building with Spills and Sewer Disposal)	Trench Recovery System with Air Stripping Treatment	1986	46 Pounds
TCAAP Total Groundwater Recovery System (Onsite and Boundary Wells-Includes Area I Well)	17 Pumpout Wells with Air Stripping Treatment	1987 (In Phases)	83,220 Pounds
New Brighton Municipal Water Supply (Data through February 1991)	Granular Activated Carbon Treatment for Existing Municipal Wells	1987	3,101 Pounds
St. Anthony Municipal Water Supply (Date through February 1992)	Granular Activated Carbon Treatment for Existing Municipal Wells	1	110 Pounds
-	Total for Groundwater Technologies	ter Technologies	86,785 Pounds
Source Area D	In-situ Volatilization	1986	130,367 Pounds
Source Area G	In-situ Volatilization	1986	97,420 Pounds
	Total for In-situ Volatilization	atilization	227,787 Pounds

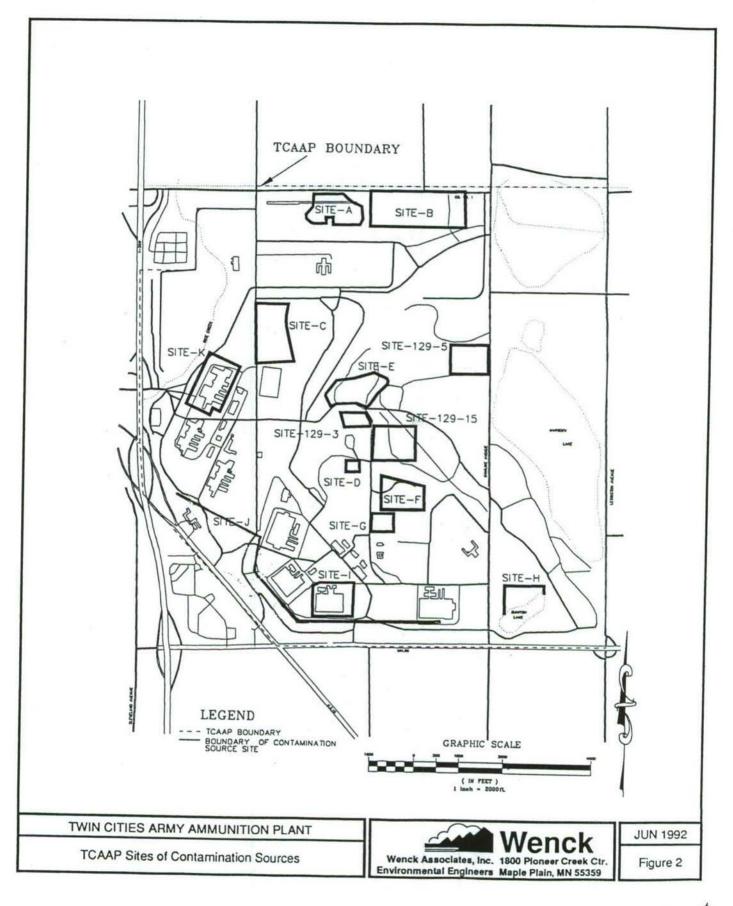
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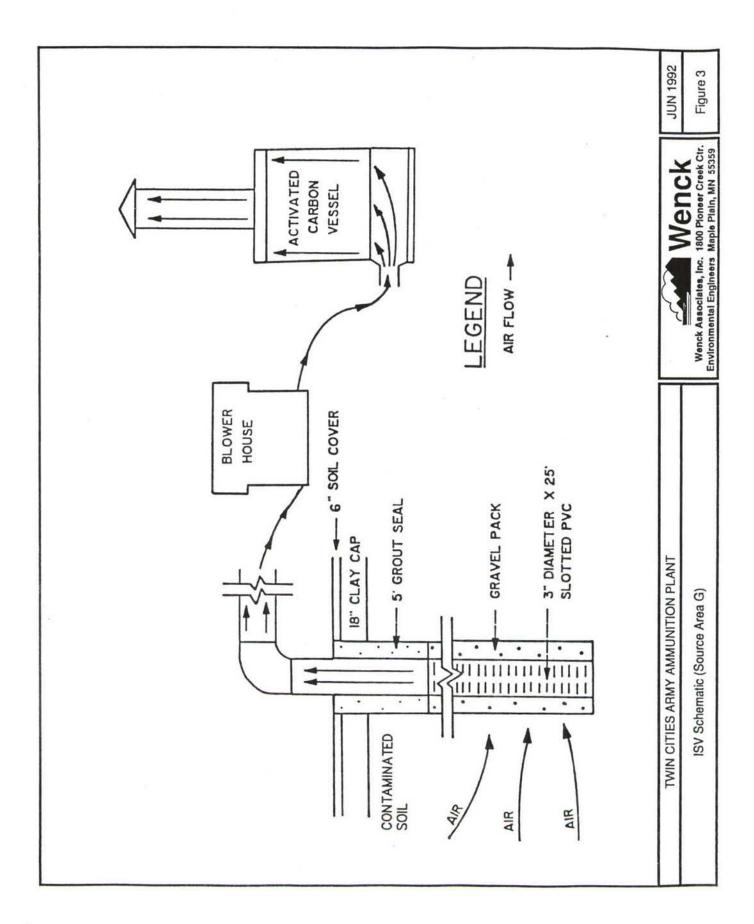
Comparison of Cost-Effectiveness of ISV and Groundwater Measures Twin Cities Army Ammunition Plant (March 1992)

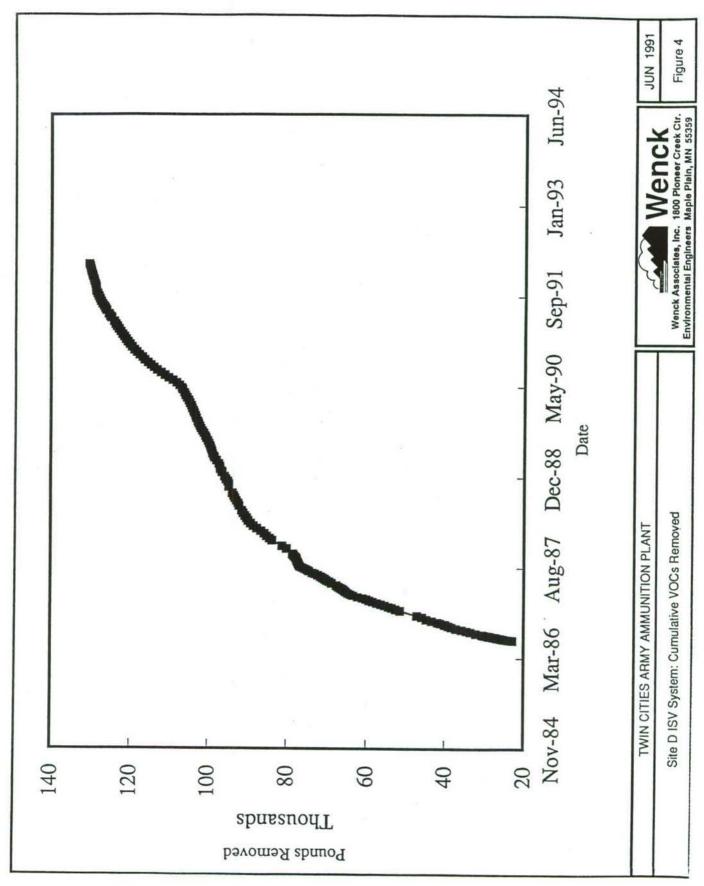
Site	Treatment	Start-up Date	Construction Cost	Operating Year	Annual O&M Cost	Pounds Removed	O&M Cost per Pound Removed
TCAAP Total Groundwater Recovery System	Groundwater Pumpout with Air Stripping	10/87	\$4,200,000	1991	000'009\$	22,940	\$ 26.15
Source Area A	Groundwater Pumpout with GAC Treatment	88/6	\$ 28,000	1989	\$ 20,800	0.97	\$21,525.00
		Tota	Total Since Start-up Through 1991	rough 1991	\$ 68,800	3	\$23,000.00
Source Area D	In-situ Volatilization	1/86	\$ 167,000	1987 1989 1991	\$ 10,900 \$ 11,400 \$ 11,400	25,918 14,991 9,134	\$ 0.42 \$ 0.76 \$ 1.25
		Tota	Total Since Start-up Through 1991	rough 1991	\$ 67,200	128,764	\$ 0.52 (Ave.)
Source Area G	In-situ Volatilization	1/86	\$ 467,000	1987 1989 1991	\$ 12,000 \$ 12,500 \$ 14,400	22,466 7,403 500	\$ 0.54 \$ 1.70 \$ 28.85
		Tota	Total Since Start-up Through 1991	rough 1991	\$ 76,900	97,310	\$ 0.79 (Ave.)

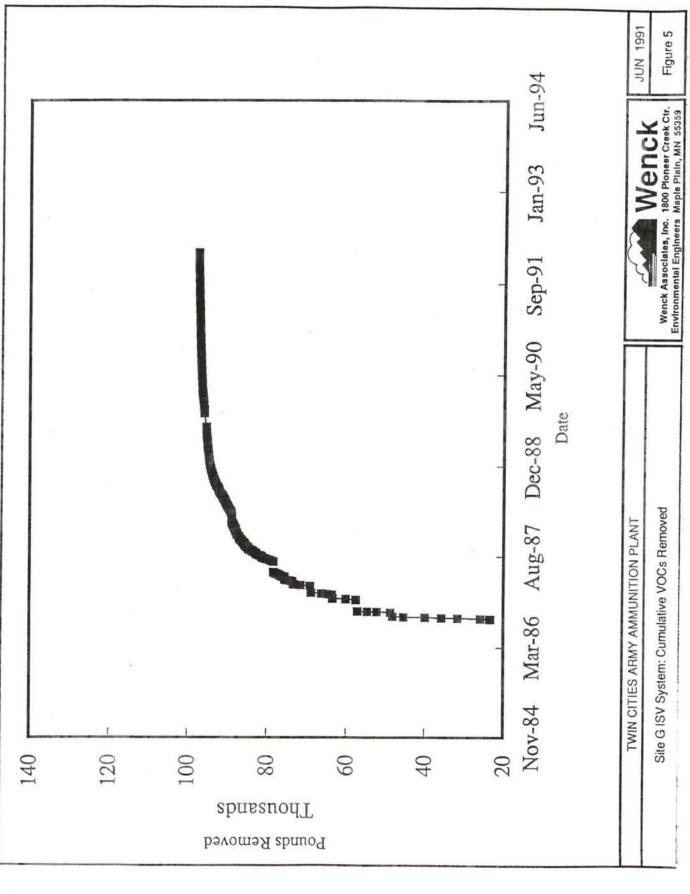


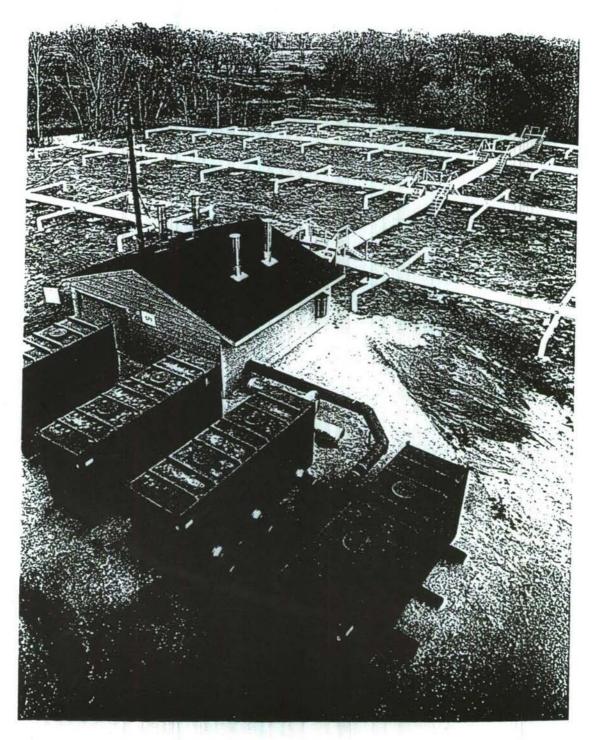












PHOTOGRAPH 1
ISV System at Source Area G
(Piping, Blower and Control Building, and GAC Units)
Twin Cities Army Ammunition Plant

CASE STUDY

ENVIRONMENTAL SITE ASSESSMENTS

FOR

DEPARTMENT OF DEFENSE BASE REALIGNMENT AND CLOSURE ACTIONS

by

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ABSTRACT

The Congress, under the Base Closure and Realignment Act of 1988 and subsequent legislation, established a procedure to evaluate the Department of Defense's mission and determine if there were excess lands or facilities which could be sold to pay realignment costs.

This paper will consist of two parts. First, it will detail the process used to characterize sites by focusing on investigations at the Indiana Army Ammunition Plant in Charlestown, Indiana. Second, the paper will also contain a summary of the investigations performed.

The Army redefined the scope of some investigations to provide more information early in the process to reduce the need for later studies. This determination was based on both economic and environmental considerations.

The ammunition plant produced large quantities of nitrocellulose and nitroglycerin-based propellants and explosives from World War II through the Vietnam War. Laboratory, testing, and burning operations were also conducted at the plant during these periods providing the potential for diverse types of contamination.

An Enhanced Preliminary Assessment (Enright et al., 1990) was prepared. A Site Investigation (SI) (CEORL, 1992) was recommended. The SI is the foundation for the statement of condition which will allow the property to be sold. This level of investigation was considered necessary by Region V, EPA. A complex chemical and biological sampling program was designed to determine whether further investigations were needed. The study team determined that additional studies were not warranted.

Introduction

The Congress, under the Base Closure and Realignment Act of 1988 and subsequent legislation, established a procedure to evaluate the Department of Defense's mission and determine if there were excess lands or facilities which could be sold to pay realignment costs. This paper is intended to provide an overview of the Base Realignment and Closure process, and to present a case study which typifies many of the environmental issues associated with selling tracts of Department of Defense land.

Background on Base Realignment and Closure (BRAC)

The history of the armed forces in the United States is, for the most part, not one of planned growth. Defense installations were historically located where they were needed as the frontier was conquered. This resulted in a patchwork system of installations which, over time, developed very strong political constituencies. Realignment of forces or closure of installations became and remains very difficult. This pattern of development has neither been cost-effective nor has it served the needs of the defense establishment.

The DoD, during the Kennedy Administration, successfully closed a number of installations. The political ramifications of these actions were tremendous. The Legislative and Executive Branches fought over base closings throughout the 1960's and the 1970's. Several legislative attempts at halting the process failed until 1977 with the passage of an act codified in 10 U.S.C. 2687. The combination of this act and the requirements of the National Environmental Policy Act (NEPA) successfully stopped all base closure efforts until passage of the Base Closure and Realignment Act of 1988 (Public Law 100-526).

The law confirmed the Secretary of Defense's action to create an independent commission to review all DOD operations. The Commission used data submitted by the four services to evaluate duplications in missions or ineffective, high-cost mission accomplishment. Commission members traveled to the field to meet local commanders and evaluate operations. This was a complex, fast-paced winnowing process to streamline DoD. The Commission recommended closing 86 installations and realigning the missions of 13 others.

A complex procedure modeled after the EPA Superfund process was initiated for identifying potential hazardous and toxic and radiological waste (HTRW) sites through preliminary assessments, then conducting remedial investigations, design and/or construction as appropriate. Subsequently, considering practical time, economic and environmental issues, the Army redefined the scope of some HTRW investigations to provide more information early in the closure process. This was designed to reduce the need for future studies and expedite the closure process. Sites where there is a low probability of significant contamination were identified, and those that could be sold without affecting mission or impacting readiness were scheduled for early disposal. Before the final sale of any Federal Facility real estate, DoD must prepare a statement of condition for the property. The sequence of investigations, remedial measures and monitoring, where necessary, become the foundation for the statement of condition about the property. The ultimate goal of this process is to have the individual state environmental protection agencies and the USEPA concur with the statement of condition. The statement of condition is published, and a public review and comment period ensue. Upon identification and resolution of pertinent comments, the DoD can then make the property available for sale.

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not burned at the plant from 1969 to 1974.

The above potential contamination sources were identified in one or more previous environmental investigations conducted for the installation. The North Ash Settling Basin, the former landfill, the Black Powder Plant wastewater treatment facilities and the P&E Sinkhole were identified as Solid Waste Management Units (SWMU's) in a 1987 report (USAEHA, 1987).

The Enhanced PA completed in 1990 indicated that all INAAP activities within the parcel were very limited in scope and duration, and that previous investigations demonstrated that there was no evidence of contamination at the potential source locations within the 860-acre parcel. However, several potential source locations within the watershed beyond the 860-acre parcel appeared to have elevated levels of some metals and polynuclear aromatic hydrocarbon compounds. The surface water drainage system appeared to be the primary migration pathway from these potential sources that could impact the subject parcel. To confirm the presence or absence of contamination on the subject parcel from the two probable source areas, the authors recommended sampling and limited chemical analysis.

Physical Setting

The terrain within the 860-acre parcel is rough. It is heavily forested and it is dissected by the downstream end of Fourteenmile Creek and its tributaries. Ground elevations range from 670 feet above MSL above the ridges to the normal low pool of the Ohio River at about 424 feet above MSL. Fourteenmile Creek has cut a steep sided, relatively narrow valley through the subject parcel. The floodplain is up to 500 feet wide on either side of the creek. Above the flood plain the valley walls are steep and exposed limestone cliffs are common. The uplands within the 860-acre parcel and beyond are flat to rolling with numerous depressions and sinkholes in certain areas.

The subject parcel is in the Central Lowlands Physiographic Province where the underlying sedimentary rock strata formed 350 to 435 million years ago during the Devonian, Silurian, and late Ordovician Geologic Periods. The rock strata in the area dip at about 25 feet to the mile to the west due to a geologic uplift zone called the Cincinnati Arch. Situated at the southern terminus of the Illinoisan and Wisconsin Till Plains, the area was also significantly impacted by the effort of ice and water working under conditions imposed by glaciation as recently as 10,000 years ago.

The underlying rock strata at the site in descending order are the: New Altany Shale, Jeffersonville Limestone, Geneva Dolomite, Louisville Limestone, and Maquoketa Group argillaceous limestones. Each of the upper three carbonate formations is exposed in various outcrops on the subject parcel. The Jeffersonville Limestone is highly susceptible to solutioning, and where it is the upper rock unit present in the area, numerous sinkholes and some caves exist. Significant weathering appears to have occurred along the interface between the Jeffersonville Limestone and the Geneva Dolomite because hundreds of springs and seeps occur during wet periods near the margin.



Four to twelve feet of very stiff glacial till or stiff to very stiff

residual silty clay soil typically exist in the uplands areas where INAAP development has occurred. The soils in the steeply sloping areas that comprise the walls of the Fourteenmile Creek valley are generally less than two feet in thickness, and they are comprised of medium stiff to stiff dark brown organic silty clays with numerous rock fragments. The soils in the low lying areas of flood plain of Fourteenmile Creek are medium stiff to stiff alluvial clays that extend to shale bedrock up to 20 feet deep.

Fourteenmile Creek drains approximately 130 square miles, of which, approximately 2500 acres lies at the downstream end within INAAP. The McAlpine Pool on the Ohio River controls the surface water elevation of Fourteenmile Creek through the INAAP property, and overbank flooding frequently occurs along Fourteenmile Creek due to backwater from the Ohio River. Nearly stagnant flow conditions occur by the late summer in Fourteenmile Creek, and its tributaries dry up.

Almost 6000 people reside in Charlestown, which borders INAAP to the northwest. Their water supply comes from an alluvial well system along the Ohio River beginning approximately 1.5 miles south of the Fourteenmile Creek confluence with the Ohio River. A deep limestone aquifer exists beneath INAAP, generally near the Ohio River elevation; however, there are no known drinking water supply wells drawing from this aquifer in the study area due to the plentiful groundwater supply nearby in the Ohio River alluvial aquifer system. A few domestic wells of limited capacity exit upgradient of INAAP in the Fourteenmile Creek Basin, near the creek where rock fracturing is more prominent and alluvial and colluvial deposits have formed.

The INAAP Natural Resources Management Plan has been used to manage the 860-acre parcel and surrounding undeveloped sections of INAAP. This management has included controlled timber harvesting, grazing, farming, fishing and hunting.

Planning The Site Investigation

Because of the large areal extent, the early portions of the SI were focused toward an extensive document review and thorough site reconnaissance. Special emphasis was placed on the site reconnaissance because of the Karst topography in the upland areas of the watershed and the potential for dumping in the sinkholes. Hundreds of sinkholes were inspected in the uplands areas, and hundreds of seep locations were observed along the walls to the Fourteenmile Creek valley. The most prominent springs were subsequently inventoried and mapped as part of the SI.

A project team from the Louisville District of the Corps of Engineers developed a proposal to do the SI with additional sampling locations and an expanded list of analytical parameters as compared to the recommendations in the Enhanced PA. The objectives of the study were to provide a comprehensive site characterization with sufficient data to determine if the subject parcel had been contaminated from operations at INAAP, and to determine whether a Remedial Investigation/Feasibility Study or no further environmental study should ensue prior to sale of the parcel. The SI was designed to test the null hypothesis, "No significant level of contamination exists within the subject parcel from operation of the INAAP."

To test the "null hypothesis" an integrated experimental sampling and analysis plan containing chemical, biological, geological and statistical components was designed and implemented by a team of scientists, engineers and technicians from the Louisville District. Redundancy was built into the design by separately examining algae, soil, sediment and water chemistry along with algae and macroinvertebrate community population density, structure and diversity. Additionally, acute and chronic laboratory sediment toxicity analyses were conducted, and they were supplemented with chemical analysis of tissue from fish exposed to the chronic sediment toxicity test.

Sediments were a primary focal point of the SI because they typically serve as the ultimate sink where inorganic and many organic contaminants tend to accumulate. Given the length of time since active operations, and the long distances between the potential source locations and the subject parcel, discovery of high concentrations of chemical contaminants was not anticipated. Therefore, examination of the algae, and the macroinvertebrates was undertaken to assess the biota at the base of the food chain which live and interact within the site media most conducive to the accumulation of contaminants.

Sample site selection was not random. The intent was to sample at the locations most likely to be contaminated. Because of the size and complexity of the study area, the total number of samples and the final selection of locations was based on the extensive field reconnaissance, which included a survey of all the sinkholes and springs in the area by a geologist who has specialized in Karst topography. The selection of chemical analytes was based on review of the materials produced and used at INAAP in conjunction with a review of the sampling and analysis results from the previous investigations. The sampling media and analytes are summarized in Table 1; and the actual sample locations for this Site Investigation are depicted on Figure 1.

Sampling and Analysis

The greatest potential sources of contamination to the subject parcel: the P&E Sinkhole; the Old landfill; The North Ash Settling Basin; and a portion of the Black Powder Plant are located in the Lick Creek watershed. Therefore, approximately one third of the sampling locations were within the watershed but outside the subject parcel. Background conditions were determined with about 10% of the sample locations selected upgradient of the subject source parcel in Fourteenmile Creek. The only potential of contamination on the subject parcel was the former Burning Ground. About 20% of the sample locations were located there. The remaining third of the samples was distributed within the subject 860-acre parcel.

All sampling and chemical analyses were conducted employing appropriate protocol and test methods in general conformance with USEPA guidance for RI/FS level investigations.

Results of the chemical analyses of the soils and sediments were evaluated relative to available standards. The USEPA Office of Solid Waste proposed a comprehensive set of action level concentrations for chemical

FIGURE 1. Sample Location Plan

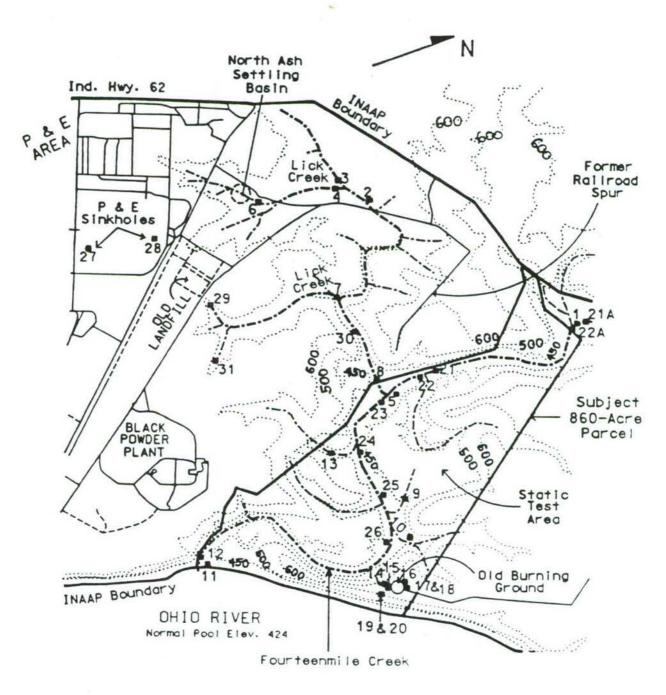




TABLE 1

NUMBER	LOCATION	MEDIA	ANALYTES
1	14 Mile Creek	Sediment Water	TCL, Metals, P&E, G Metals, (Total & Dissolved,
2	Lick Creek Trib.	Sediment	TCL, Metals, P&E, G Metals, (Total & Dissolved,
3	Lick Creek Trib.	Water Sediment	TCL, Metals, P&E, G
4	Lick Creek	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
5	14 Mile Creek	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
6	North Ash Basin Drain	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
7	Lick Creek Trib.	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
8	Lick Creek	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
9	14 Mile Creek Trib.	Water Sediment	Metals, (Total & Dissolved, TCL, Metals, P&E, G
		Water	Metals, (Total & Dissolved,
10	McCormick Branch	Sediment Water	TCL, Metals, P&E, G Metals, (Total & Dissolved,
11	Ohio River	Sediment Water	TCL, Metals, P&E, G Metals, (Total & Dissolved,
12	14 Mile Creek	Sediment Water	TCL, Metals, P&E, G Metals, (Total & Dissolved
13	14 Mile Creek Trib.	Sediment Water	TCL, Metals, P&E, G Metals, (Total & Dissolved
14	Burning Ground	Soil	TCL, Metals, P&E, G
15	Burning Ground	Soil	TCL, Metals, P&E, G
16	Burning Ground	Soil	TCL, Metals, P&E, G
17	Burning Ground	Soil	TCL, Metals, P&E, G
18	Burning Ground	Soil	TCL, Metals, P&E, G
19	Burning Ground	Soil	TCL, Metals, P&E, G
20	Burning Ground	Soil	TCL, Metals, P&E, G
21	14 Mile Creek	Sediment	TCL, Metals, P&E, G
		Water Biota	Metals, (Total & Dissolved Metals
21A	14 Mile Creek	Sediment	TCL, Metals, P&E, G
22	14 Mile Creek	Biota	Metals
22a	14 Mile Creek	Sediment	TCL, Metals, P&E, G
23	14 Mile Creek	Sediment	TCL, Metals, P&E, G
		Water Biota	Metals, (Total & Dissolved Metals
24	14 Mile Creek	Sediment Biota	TCL, Metals, P&E, G Metals
25	14 Mile Creek	Sediment Water Biota	TCL, Metals, P&E, G Metals, (Total & Dissolved Metals
26	14 Mile Creek	Sediment Biota	TCL, Metals, P&E, G Metals
27	CC Dryer Cave	Sediment	TCL, Metals, P&E, G Metals, (Total & Dissolved
28	P & E Sinkhole	Water Soil	
29	Old Landfill Drain	Sediment	TCL, Metals, P&E, G TCL, Metals, P&E, G Metals, (Total & Dissolve)
30	Lick Creek Spring	Water Sediment	Metals, (Total & Dissolve TCL, Metals, P&E, G
31	Lick Creek Trib.	Water Sediment Water	Metals, (Total & Dissolve TCL, Metals, P&E, G Metals, (Total & Dissolve

TCL - Target Compound List
P&E - Propellants and Explosives
DO - Dissolved Oxygen
SC - Specific Conductance
G - Grain Size



Table 1 Sample Points, Media, and Analyses

contaminants in soils, water, and air in the Federal Register, dated July, 1990 (USEPA, 1990). These risk-based action levels were used as standards to evaluate the chemical concentrations in the soils analyzed from the old Burning Ground. Sediments were evaluated relative to standards for the pollutional classification of sediments published by USEPA (USEPA, 1977) and the Illinois EPA (Kelly and Hite, 1984). Unlike the proposed soil standards, the sediment criteria are not based on an assessment of risk to human health or the environment. They simply provide a qualitative basis for classification of the sediments.

The soil or sediments from locations 1 through 31 were all analyzed for the presence of propellant and explosive compounds, metals, PCB's, and the USEPA Target Compound List of Volatile and Semivolatile organic compounds. Selected locations were sampled for nutrient analyses. Some of these locations were sampled during both the fall and the spring, and analyzed for total metal content. No propellant or explosive compound from a list of the thirteen most common excitable compounds was detected in any of the soil or sediment samples.

Trace concentrations of polynuclear aromatic hydrocarbons (PNA's), base/neutrals, and/or volatile organic compounds (VOC's) were detected in some of the sediments analyzed. Fluoranthene and Pyrene were detected at three upgradient locations in the Lick Creek watershed at concentrations less than 1 microgram per gram (ug/g).

Several phthalate compounds were detected in soil or sediment, but the probable source appeared to be laboratory contamination during the extraction process. Up to three of the five following compounds: acetone, 2-butanone, toluene, methylene chloride, and xylene were detected in 7 samples at concentrations between 2 and 100 micrograms per kilogram (ug/kg). The methylene chloride, which is the least biodegradable of the analytes detected, was found at sample location 1, upstream of the area to be sold, in Fourteenmile Creek. No other samples contained the compound. The highest levels of acetone and 2-butanone were found at sample location 11 (the Ohio River). A possible source of these contaminants is the backflow of the Ohio River onto INAAP property. Trace amounts of toluene, xylene, and 2-butanone were found in Lick Creek, but at levels far below the EPA proposed action levels mentioned previously.

Samples from locations 1 through 13 were analyzed for nutrients, and samples from all 31 locations were analyzed for metals. Total phosphorus concentrations were found to be slightly elevated, in 12 out of 15 samples (includes two split samples), according to IEPA's standards, while according to the USEPA criteria two of the samples classify as moderately polluted and two classify as heavily polluted. The rest classify as non-polluted for phosphorus. Total Kjeldahl Nitrogen (TKN) was categorized as non-elevated according to IEPA criteria and nonpollutioned according to the USEPA criteria. Ammonia concentrations were classified as nonpolluted according to the USEPA criteria.

To assess the results of the chemical analyses of soils from the former burning ground, the statistical methods used by USEPA to evaluate a solid waste were applied. The USEPA Office of Solid Waste Proposed Action Levels (USEPA, 1990) were used as the applicable regulatory threshold values. Mean,

analyte. Then a theoretical value above the mean was calculated as the upper confidence level concentration using a "student t" probability distribution. It can be stated at a 90% confidence level that the actual mean does not exceed this value. This calculated upper confidence level concentration was compared to the regulatory threshold values available. Proposed action levels were available for arsenic, beryllium, cadmium, chromium, mercury, and nickel. With the exception of beryllium, all calculated upper confidence level concentrations were well below the proposed action levels. Beryllium exceeded the proposed action level, but it appears to occur naturally in the area soils at levels above USEPA's proposed action levels. No action levels were available for aluminum, copper, iron, lead, manganese or zinc.

Box plots were used to provide a graphical interpretation and basis for comparison of the concentrations of metals in the sediments from each of four subdivided areas: background; Ohio River; Lick Creek watershed; and the subject parcel. The plots also displayed the available classification criteria concentrations developed by the Illinois EPA and the USEPA. Box plots including 95% confidence intervals were used also to explore spatial and temporal variability and to graphically perform a simple yet effective non-parametric analysis of variance. An example box plot, Figure 2, demonstrates the spatial and temporal distribution of chromium in the sediments throughout the study area. To develop this plot an asymptotic, Gaussian-based estimation of the standard deviation (S_{med}) of the median (M) was calculated as shown below:

$$S_{\text{med}} = 1.25 \frac{R}{1.35\sqrt{n}}$$

"R" is the interquartile range, or the value of the 75th percentile minus the 25th percentile. The 95% confidence interval for the median is then calculated as:

$$CI_{med.95} = M \pm C(S_{med})$$

"C" is a constant which equals 1.7 for the 95% confidence interval.

The range of the data is displayed as lines drawn up from the 75th percentile and down from the 25th percentile. A convenient method for evaluating outliers is also included in these icons. Limits, called fences, are calculated based on the distribution of the data. Values which fall outside these limits are uniquely displayed. Two such limits, the inner fence and the outer fence, are calculated. Values which fall beyond the inner fence, but not beyond the outer fence, are displayed with asterisks. Values outside the outer fence are displayed as circles. The results of analyzing the sediment data were that metals concentrations appear to be consistently higher than background levels in the upper Lick Creek basin, but there is no conclusive evidence to suggest that there is contamination in Fourteermile Creek.

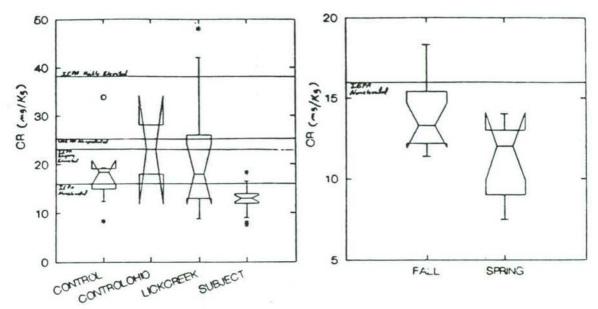


FIGURE 2. Box Plots of chronium distribution. The plot on the left graphically compares the distribution of chronium concentrations throughout the study area by locational subset. Control refers to the set of data from from sample locations 1, 21A, and 22A. Control Ohio refers to the data set from sample locations 11 and 12. Lick Creek refers to the data set from sample locations 2-4, 6-8, and 27-31. Subject refers to the data set from sample locations 5, 9, 10, 13, 21, 23, 24, 25, and 26. The box plot on the right subdivides and compares the data from the subject parcel temporally.

The potential for temporal changes in sediment chemistry were examined because of the physical differences in flow conditions (and therefore sediment deposition) between the periods of heaviest rainfall in winter and spring and the driest time of the year in summer and fall. The median concentrations were generally zero to forty percent higher in the fall, but the range or variability of concentrations was consistently greater in the spring.

Water was identified as the primary transmission medium, in which contaminants can migrate from potential source areas on the INAAP property. Water samples were acquired in the spring when groundwater percolation from springs in the walls of Fourteenmile Creek Valley was actively occurring. The points in time selected for sampling water (spring) were considered to be the most probable times for migration of contaminants from the potential source areas to the subject parcel.

The water sampling was conducted in the winter and spring, and, as expected, no dissolved oxygen problems were observed. Concentrations of total and dissolved solids and chlorides and sulfates were below drinking water criteria, but the highest solids, chloride and sulfate values were specific to the Lick Creek drainage area. Iron and manganese were detected

at concentrations slightly above water quality criteria at locations 21, 23, and 25 within the subject parcel, and significantly higher levels were detected at locations 2, 3, 4 and 6, immediately down gradient of the North Ash Settling Basin and the old Landfill in the upper Lick Creek drainage area.

Artificially cultivated periphyton, were used to assist in the contamination assessment of Fourteenmile Creek. This method provided added resolution when used with chemical analyses of soils, sediments, and water. This increase in resolution results from the tendency of these organisms to bioaccumulate various elements and compounds and store them in vacuoles, fatty or oily deposits, and/or tissue at far greater concentrations than are present in the surrounding environment. The result of such bioaccumulation can be manifested in altered growth rates, altered community structure, decreased densities, or simply in the concentration of these metals in periphytic cytoplasm; therefore, algae growth rates, community structure, and cell densities were analyzed from samples taken throughout Fourteenmile Creek. Chemical analysis for bioconcentration of metals was also performed on the algae samples.

Analysis of phytoplankton revealed few truly planktonic species. High water events immediately prior to the study and during the study maintained a diverse tychoplanktonic community which accounted for the high diversity observed on the clay tile collection media used to sample the algae.

Periphyton densities increased slightly throughout the study. Comparison of densities between control sites and suspected impact sites indicated significantly greater densities in the impact areas. A potential explanation of this phenomenon is that more intense shading upstream may have occurred with the increase in spring foliage. The upper part of the creek was more densely wooded, apparently because it is less subject to the back water flooding of the Ohio River.

Another biological method employed to assess the effects of the INAAP operations on the subject parcel was a study of macroinvertebrates. Invertebrates were sampled using Hester-Dendy multiplate samplers. No significant difference in macroinvertebrate density was observed between sites immediately upstream and downstream of Lick Creek. However, macroinvertebrate density was significantly greater in the far downstream sites.

Oligochaete density was greater at upstream sites while chironomid density was greater in downstream sites. Ratio of chironomids to oligochaetes did not differ significantly between immediate upstream and downstream sites. Ratio of chironomids to oligochaetes at the far downstream site was significantly greater. There were no significant differences in densities of oligochaetes or chironomids between sites immediately upstream and downstream of Lick Creek. Density of chironomids was significantly greater and density of oligochaetes significantly less in the far downstream site compared to either site immediately upstream or downstream of Lick Creek.



There was no evidence that effluent waters from INAAP have a negative impact on macroinvertebrates. Macroinvertebrate communities appear to be affected more by backwash waters from the Ohio River.

An integral part of the biological analyses performed for this investigation was an examination of sediment toxicity and bioconcentration. The rationale for selection of sample locations for toxicity analyses was the same as for the evaluation of the macroinvertebrate community.

Two species Hyalella Azteca (a fresh water amphipod) and Pimephales Promelas (fat head minnows), were selected for acute and chronic laboratory sediment toxicity testing. This testing consisted of exposing the test species to site sediments in laboratory aquaria for 10 days (acute test) and 31 days (chronic test). Mean survival rates for both species in both groups of tests were greater than 90 percent, indicating no apparent toxicity. Bioaccumlation of metals and PCBs was assessed through chemical analysis of tissue from the fat head minnows subjected to the chronic test. No PCBs were detected; however, barium, copper, lead, mercury, silver, and zinc were detected. However, this data did not refute the "null hypothesis" because there was no apparent difference in tissue concentrations between the control and impact sites.

SUMMARY

There was minimal visible evidence of human impacts within the 860-acre subject parcel. The only exceptions were building remnants at the former Static Test Area and Rose Island Amusement Park, trenches at the former Burning Ground and fisherman's debris in Fourteenmile Creek.

No evidence of the release of propellants and explosive materials, PCB's, or pesticides from any of the potential source locations in the Fourteenmile Creek watershed was found. Some trace amounts of PNA's were found, which is most likely attributable to material contained in the North Ash Settling Basin. However, these amounts were not significant, and these analytes were not detected within the subject parcel. The trace levels of the base/neutral compounds detected were phthalate compounds, which were probably detected due to laboratory contamination in the extraction process. The trace levels of VOC's that were found; acetone, 2-butanone, methylene chloride, toluene, and xylene, were all well below EPA proposed action levels (USEPA, 1990). The majority of these detections were attributable to impacts to the subject parcel from the Ohio River. No other organic contaminants were detected.

There is evidence in the water chemistry data of the potential release of sulfate and phosphate from either, or perhaps both the North Ash Settling Basin and the Old Landfill to Lick Creek, but the concentrations detected were well below water quality standards. The levels of these parameters for the waters within the subject parcel are less than the levels in both Lick Creek and the Ohio River, which tends to confirm the "null hypothesis."

There appears to be slightly elevated levels of chromium, iron, manganese, and zinc in soils from the Old Burning Ground above background soil concentrations. Neither the mean value nor the calculated upper 90

percent confidence limit value for the mean exceeded the USEPA proposed action levels for any analyte except beryllium. Naturally occurring beryllium in the region exceeds the proposed action levels.

There is evidence of release of some metals from the potential source areas in the Lick Creek watershed. Elevated levels of arsenic, cadmium, chromium, iron, lead, and manganese were found in the Lick Creek watershed sediments. Elevated cadmium, chromium, iron, lead, mercury, and zinc levels were also detected at the confluence of Fourteenmile Creek with the Ohio River. Background concentrations of cadmium, chromium, and iron also appeared slightly elevated. Cadmium is the only metal which appeared elevated within the subject parcel, with iron also considered slightly elevated. Although the cadmium concentrations on the subject parcel appear somewhat higher than the background, they are very similar when compared to the Lick Creek and Ohio River data. The analysis of sediments confirmed that potential sources of contamination exist in the Lick Creek watershed; however, there was no evidence to support a conclusion that the subject parcel has been contaminated by the potential source areas within the watershed.

The periphyton community appeared healthy for the biological parameters of community structure, cell densities, and growth rates. Examination of the periphyton for metals accumulation revealed evidence of some bioaccumulation of arsenic, barium, chromium, copper, and zinc in Fourteenmile Creek. However, there were no statistically significant differences between the control and impact locations.

The analysis of macroinvertebrates for standard biological indices indicated that Fourteenmile Creek within the subject parcel supports a healthy and vibrant macroinvertebrate community. There appears to be a stimulatory effect on the macroinvertebrate population from the Ohio River, but there was no indication of adverse impacts to Fourteenmile Creek from its junction with Lick Creek.

Analysis of sediments for acute and chronic toxicity indicated no significant mortality in any of the tests, and no significant differences between the background and subject parcel locations. However, there did appear to be significant uptake or bioconcentration of copper in the fish exposed to sediments from the subject parcel in the chronic toxicity tests. There are numerous variables which can affect uptake and bioconcentration of contaminants, but the sample and analysis design attempted to keep these variables constant between sample locations and analyses. Analyses of the sediment chemistry indicated non-elevated concentrations of copper in both the background and subject parcel locations. Since the uptake of copper was not apparent in tests from the background or control area and the total concentrations of copper in the sediments are similar, some change of conditions may occur in Fourteenmile Creek within the subject parcel which increases the bioavailability of the copper. Unfortunately, there was inadequate sample volume to perform a confirmatory tissue analysis. Although some anomalies are present in the Site Investigation data, the redudancies built into the investigation provide convincing confirmation of the "null hypothesis". No significant level of contamination exists within the subject parcel from operation of INAAP. No further environmental investigation was recommended.

Conclusions

- 1. There are a variety of complex issues associated with conducting contamination assessments for base closure actions. Usually the sites are relatively large, and they typically have a complex history combined with poor or inadequate documentation to trace hazardous substances used, wastes generated and ultimate waste disposal practices.
- 2. Compounding these circumstances are the overlapping array of federal and state regulatory standards. The high rate of personnel turnover and inadequate staffing at the federal and state regulatory agencies often inhibits regulatory support during the planning stages of an investigation. It also critically affects the quality, consistency and expendiency of regulatory review and comment.
- 3. Because of the large quantities of data generated in one of these investigations, statistical correlation is necessary to interpret the data. Using appropriate statistical methods, in the sampling design makes the data more defensible. It allows better quantification of risks, and facilitates optimal use of sampling and analysis funds.
- 4. An interdisciplinary team that includes represention of ecological or biological scientists along with the more typical geologists, chemists and engineers is critical for investigations of large tracts of land.

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FORT ORD SUPERFUND SITE: AN APPROACH TO AN ACCELERATED REMEDIAL INVESTIGATION/FEASIBILITY STUDY

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INTRODUCTION

Fort Ord, a U.S. Army base in Monterey County, California was placed on the National Priorities List of Hazardous Waste Sites on February 21, 1990. A Federal Facilities Agreement (FFA) was signed by Fort Ord for the U.S. Army with the U.S. Environmental Protection Agency, Region IX, the California Department of Health Services, and the California Regional Water Quality Control Board, Central Coast Region in July 1990. The FFA, consistent with the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), outlines a phased remedial investigation/feasibility study (RI/FS) to be completed in November 1995 and remedial action to begin in February 2000. However, subsequent to the FFA, Fort Ord was placed on the 1991 Base Realignment and Closure (BRAC) List. The inclusion of Fort Ord on the BRAC list and the subsequent passage of legislation requiring acceleration of the RI/FS process (36 months) presented the difficult challenge of developing a new CERCLA approach to meet all the various program needs.

Fort Ord, the Sacramento District Army Corps of Engineers, and Harding Lawson
Associates developed a non-traditional CERCLA program to meet the mandated three year
RI/FS schedule and BRAC objectives. This program includes foregoing a formal phased
program for what has been termed a continuous or rolling RI in conjunction with an enhanced
feasibility study, remedial design and remedial action program. The program also excludes from

the complete CERCLA process many of the 28,000 acres that comprise Fort Ord thought not to be impacted by activities which may result in hazardous and toxic waste.

The key elements for acceleration of the CERCLA process include:

- development of a risk based investigation approach to evaluate contaminant transport mechanisms and source areas simultaneously
- A rolling RI that includes individual site schedules and future work plans in the investigation reports
- use of a low cost screening risk evaluation to exclude sites from the RI process and develop cleanup levels
- o innovative approaches to remediate sites while conducting the investigation
- an enhanced FS, remedial design and remedial action program that includes combining and overlapping phases.

This alternative approach presented will allow for expediting the characterization and cleanup of contaminated sites within Fort Ord to 1) protect human health and the environment, 2) meet the congressionally mandated 36-month RI/FS schedule, 3) meet a primary BRAC objective of identifying clean parcels of land for reuse, and 4) reduce the funds required to complete the CERCLA process.

BACKGROUND

Although the emphasis of this paper is the acceleration of the CERCLA process, it is important to have some basic background information on Fort Ord. Certain information presented in this section, including Fort Ord location and history, hydrogeology, and remediation history are key factors in the acceleration process.

Fort Ord Location and History

Fort Ord is located adjacent to Monterey Bay in northwestern Monterey County,

California, approximately 80 miles south of San Francisco (Plate 1). The base comprises

approximately 28,000 acres adjacent to the cities of Seaside, Sand City, Monterey, and

Del Rey Oaks to the south and Marina to the north. Included within the Fort Ord boundaries is

approximately 4 miles of Monterey Bay shoreline. Laguna Seca Recreation Area and Toro

Regional Park border Fort Ord to the south and southeast, respectively. Land use east of Fort Ord is primarily agricultural, as was land use at Fort Ord before the Army acquired the property.

Since its opening in 1917, Fort Ord has primarily served as a training and staging facility for infantry troops. No permanent improvements were made until the late 1930s, when administrative buildings, barracks, mess halls, tent pads, and a sewage treatment plant were constructed. From 1947 to 1975, Fort Ord was a basic training center. Before 1947 and after 1975, the 7th Infantry Division (Light) occupied Fort Ord. Light infantry troops are those that perform their duties with very little support equipment allowing rapid deployment to where ever needed.

The three major developed areas within Fort Ord are the Main Garrison, the East Garrison, and Fritzsche Army Airfield (FAAF). The remaining approximately 20,000 acres of undeveloped property are used for training activities. The Main Garrison contains commercial, residential, and light industrial facilities. It was constructed between 1940 and the 1960s, starting in the northwest corner of the base and expanding southward and eastward. During the 1940s and 1950s, there was a small airfield in the central portion of the Main Garrison. This airfield was decommissioned when FAAF was completed, and the airfield facilities were redeveloped as motor pools or for other operations. FAAF, which serves as the general airfield for Fort Ord, is in the northern portion of the base, adjacent to the city of Marina. FAAF was incorporated into Fort Ord in 1960 and expanded in 1961. The East Garrison occupies 350 acres on the northeast edge of the base and consists of military and industrial support areas, recreational facilities, and recreational open space.

Regional Geology/Hydrogeology

Fort Ord is within a geologically complex area in the central California Coast Ranges.

The Salinas Basin and the Seaside Basin are the two main hydrogeologic structures underlying

Fort Ord. The Salinas Basin underlies the northern part of Fort Ord; the southern,

approximately two-thirds of the base is underlain by the Seaside Basin. The location and characteristics of the boundary between these two basins is uncertain.

In the area of Fort Ord, there are four relatively well-defined aquifers within the Salinas Basin: the A-, 180-, 400-, and 900-foot aquifers. The latter three aquifers were originally named to reflect the average depth to water in each. Groundwater supply wells for Fort Ord and neighboring communities are completed in the three lowest aquifers.

The Seaside Basin reportedly consists of the four aquifers; however, on the basis of the limited data available for the Seaside Basin, the water-bearing zones of this basin do not correlate well with those of the Salinas Basin.

Characterization/Remediation History

The first environmental investigation conducted at Fort Ord began in 1984 at the Fritzsche Army Airfield Fire Drill Burn Pit. Investigation of the Fort Ord landfills began in 1986. Groundwater contamination linked to the landfills was the driving force behind the EPA conducting the Hazardous Ranking Survey which resulted in the listing of Fort Ord on the National Priorities List. These two sites are now operable units in the advanced stages of the CERCLA process. A groundwater and soil treatment system was constructed at the Burn Pit site in 1988. Approximately 4,000 cubic yards of contaminated soil were treated and groundwater cleanup is ongoing. This soil treatment system has been proposed for use in treating hydrocarbon-contaminated soil from future remediation activities.

By 1991, a total of 17 site characterizations had been conducted at Fort Ord. Fort Ord was placed on the NPL and the FFA was signed in 1990. The FFA originally structured the CERCLA program for Fort Ord following standard guidelines for a phased approach. This phased approach, shown on Plate 2, required significant site characterization prior to evaluation of potential contaminant transport mechanisms, and included all potential contaminant source areas (sites) into the full CERCLA process. In early 1991, when Fort Ord was identified as a potential installation for BRAC listing, the Fort Ord Team, consisting of the Fort Ord

Environmental staff, Sacramento District, U.S. Army Corps of Engineers (USACE), and Harding Lawson Associates, developed an alternative approach to the standard CERCLA process, and submitted revised work plans to the regulatory agencies proposing this alternative approach. The alternative approach, termed a Risk-Based Approach (described below), was presented to the parties of the FFA in the Summer 1991. It was approved in the Fall of 1991, and is currently being implemented.

Site Identification

Preliminary evaluation of installation activities that could pose potential environmental problems identified 39 sites for investigation under CERCLA and several additional sites requiring evaluation under the RCRA-CERCLA integration requirements. These site, have been segregated into three groups on the basis of the types of contaminants which may be present: 1) petroleum hydrocarbons 2) solvents, metals, or pesticides 3) other contaminants (i.e, explosive compounds). The majority of the sites appear at this time to be soil contaminated with petroleum hydrocarbons. The remainder of the sites contain soils with either solvents, metals or other contaminants, or a combination of these. Groundwater contamination exists at several sites and is generally from solvents or petroleum hydrocarbons.

CERCLA ACCELERATION MEASURES

Acceleration measures for the Fort Ord CERCLA process include those currently being implemented and those to be employed in the near future. These measures are discussed in detail below. Plate 3 presents a matrix showing the various acceleration measures being used or proposed for the Fort Ord program and their applicability to the sites being investigated.

Current Acceleration Measures

The acceleration measures presented below have been agreed to by the parties of the FFA and are currently being implemented.

Risk-Based and Rolling RI

The classical RI/FS approach is a stepped approach in which the RI first evaluates the potential source areas and then, using data generated in the source area investigations, looks at potential receptors and the associated contaminant migration pathways. This approach tends to result in a lengthy process with work at some locations retarded by more complex and time-consuming work at other sites. Ultimately operable units are developed to minimize the potential time conflicts between sites with different investigation requirements, but this step can take several years and several phases of work.

To reduce this lengthy process, the approach developed for Fort Ord simultaneously evaluates both migration pathways for potential receptors and the potential source areas. This approach has been termed a risk-based approach since it emphasizes an initial understanding of potential receptors and their associated risks rather than just studying sites. Site investigations are then prioritized on the basis of the types of possible contaminants and associated toxicity, and potential impact to receptors. Additionally, each potential source area is evaluated independently, based on the prioritization and as funding allows, using an approach termed the rolling RI.

The rolling RI approach allows for site characterization activities to progress independently for each site. Since basewide studies, developed to understand the site-wide hydrogeology, soils, and background chemistry, are proceeding concurrent but independent to the site characterizations, schedules do not need to be tied to other activities. Therefore, as a phase of work is completed for a site, the appropriate report can be generated and the site can proceed into the next phase of work, independent of the progress of other site characterization activities. This approach allows clean sites to be more quickly identified and lesser contaminated sites to be cleaned up while other more contaminated sites undergo additional RI activities.

An important benefit of this approach is that some sites will not need to complete the full CERCLA process and are deleted or cleaned up prior to reaching the FS stage. Sites that

require an FS will be handled similarly to the rolling RI; independent schedules will be used to accelerate the FS process.

Reporting and Review

Reports are standardized to assist regulatory review of multiple reports. Next phase work plans are included as appendices to the independent site reports eliminating the need for extra documents and the associated regulatory review. Regulatory review is also accelerated by conducting summary presentations of investigation results prior to report submittal to resolve potential controversial issues.

Document review times are documented by using the U.S. Army Corps of Engineers

Automated Review Management System (ARMS) to store and transmit comments, ultimately
decreasing review times by accelerating comment transmittal. The regulatory agencies have also
agreed to use this system to provide timely comments.

Investigation Procedures

Because of the large number of sites with similar types of potential contaminants, guidelines were established for investigating similar potential sources. These guidelines provide consistency from site to site and simplify the review process. The guidelines are negotiated with and approved by the regulatory agencies prior to work plan development.

Innovative investigation techniques are also used to accelerate the investigation process. Several techniques that have proved successful are the use of surface geophysics to delineate landfill or subsurface hydraulic barriers and the use of specialized drilling methods to minimize the number of time consuming and expensive deep wells (i.e., Hydropunch). Pilot borings that can be quickly drilled and sampled using standard innovative techniques (i.e., Hydropunch) and then geophysically logged and converted to piezometers are regularly used to provide hydrogeologic data.

Site Elimination Actions (SEAs) are conducted as part of the investigation approach.

For sites with little or no contamination, SEA activities are conducted as part of the

investigation to show that the site does not present a risk to human health or the environment. One example of a SEA is utilization of a technique referred to as "investigation by excavation". If a limited area of contamination is suspected, the bounds of the contamination are determined by excavation. Excavation ceases when soil contaminant levels reach a predetermined level, referred to as a target level, which has been calculated prior to excavation using standard risk assessment procedures as being protective of human health and the environment. Investigation by excavation to calculated target levels allows the site to be cleaned up during the investigation phase with only a follow-up report to verify site completion. For sites where data suggests that contamination is not a problem, the site data is evaluated using a Screening Risk Assessment (SRE). The SRE is used to calculate the target cleanup levels or to show that residual levels or non-detect levels are protective of human health. This assessment utilizes conservative exposure scenerios and is therefore quickly produced, is cost effective, and amenable to short review time. This process helps identify clean parcels that were originally included as sites to be investigated.

Future Acceleration Measures

This section describes the measures that the Fort Ord Team believes are critical to further accelerate characterization and remediation activities at Fort Ord. These techniques have been proposed for use at the installation and are currently being evaluated by the regulatory agencies.

Enhanced Feasibility Study

As previously discussed, sites requiring feasibility studies will also utilize independent schedules. Additional acceleration of the rolling RI/FS approach occurs by enhancing the FS to combine steps and overlap phases. The enhanced FS features the following: early remedial technologies screening, inclusion of the Proposed Plan (the selected remedial alternative for the site) into the FS, and appending standard remedial design packages (with site-specific



addendum). This enhanced FS will be submitted to the regulatory agencies for review and comment and, after incorporation of their comments, submitted for public review.

The goal of the enhanced FS is to streamline the regulatory agency and public review and comment period shorter in that the evaluation (FS), selection (Proposed Plan), and design (Standard Remedial Design Package) can be reviewed at once rather than sequentially. This will greatly reduce the time required for approval of a site's remediation and accelerates this portion of the process.

Once the FS is approved by the regulatory agencies, the standard design package will be sent to preselected contractors for bidding while the Record of Decision (ROD) for the site is being prepared and approved. By the time the ROD for the site is approved, the contractor bids will have been evaluated and the contractor selected so that remedial construction will begin promptly which accelerate the process.

A more detailed discussion of the components of the enhanced FS follows.

Remedial Technologies Screening

There are numerous remedial technologies that are potentially applicable to the various types of soil and groundwater contamination thought to be present at the installation. Also, there are numerous technologies that will not be applicable or cost effective at the installation because of the type, nature, and extent of contamination; and the soil, geologic, and hydrologic conditions of specific sites within the installation. Furthermore, the concept of the rolling RI is such that a FS will be prepared for each site as its RI is completed and approved by the regulatory agencies. The site-specific RI will be immediately followed by a site-specific FS rather than the more traditional approach, where the FS that addresses all sites is presented in one document that is not prepared until all of the RI information has been collected.

Taking the above factors into consideration, a Remedial Technologies Screening (RTS) will be conducted to meet the following goals: 1) early identification of sections of those remedial technologies that might be suitable for the various types of contaminants present in soil and groundwater at Fort Ord and 2) eliminate those technologies that are not suitable. The RTS-

is intended to eliminate most of the unsuitable technologies early and enables the site-specific feasibility studies to focus only on those technologies that are potentially suitable for that site and its specific contamination problems.

The screening of the technologies in the RTS will be performed in accordance with applicable sections of the Army's guidance document AR200-2 and the USEPA's feasibility study guidance. A draft RTS will be provided to the regulatory agencies for review and comment and the document will also be provided to the public for review and comment. The comments will be incorporated into a final RTS.

The final RTS will be used as a primary guidance document when preparing the sitespecific feasibility studies. Only those technologies identified in the final RTS will be
considered for screening and subsequent combination into remedial action alternatives for the
site specific FS. This will significantly reduce the amount of time required to prepare, review,
and approve the site-specific FS.

Standard Remedial Design Package

Another proposed method to accelerate the CERCLA process is to prepare standard remedial design packages for similar soil and/or groundwater remedies. Because of the relatively uniform sandy soil conditions and the similarity of many of the contamination problems (hydrocarbons), standard remedial design packages for the selected remedial technologies can be applied to many of the sites.

Standard design packages will be developed for each of several remedial techniques for soil and groundwater. For example, a standard remedial design package will be prepared for bioremediation of hydrocarbon contaminated soils at the Fritzsche Army Airfield Soil Treatment Facility when soil excavation and biological treatment is the selected remediation for a site. If the selected remediation is insitu soil venting to remove the hydrocarbons, then the standard design package for that remedial technology would be used for that site. It is planned that the remedial design package to be used at a site will include a site-specific addendum containing

changes or specific conditions that adapts the general design package to the sites' unique conditions.

Each standard remedial design package, when amended to tailor it to the specific conditions for that site, will provide sufficient detail to serve as a bid package to pre-selected remedial contractors (discussed below). The goal of developing the standard remedial design packages and having them preapproved by the regulatory agencies is to reduce the time required between selection of a remedy at the Enhanced FS/Proposed Plan stage and the design and approval of the remedy.

Preselected Remedial Contractors

Because of the similarity of site conditions and contamination problems, only a limited number of different remediations are likely to be needed to cleanup the various installation sites. Pre-selecting licensed contractors with the capabilities to bid and construct these remedies will significantly reduce the time required to authorize a contractor to begin work in the field.

SCHEDULE

Current Schedule

Highlights from the current negotiated Federal Facility Agreement (FFA) schedule for Fort Ord are shown on the schedule comparison table below.

The FFA schedule incorporates all currently known information about potential contaminated sites at Fort Ord; new sites may be added if further information and investigation warrants inclusion in the CERCLA process.

Schedule Acceleration

An accelerated schedule, Revision I, was in development by the installation in May 1991 to address Base Realignment and Closure (BRAC) concerns. The acceleration was achieved through 1) reducing contracting periods resulting from competitively soliciting each phase of the

work effort, and procuring only one firm to carry out all necessary actions up to construction contract award, and 2) by eliminating a formal submittal of an installation-wide planning document midway through all field work, and replacing it with individual submittals tailored to each site or identified OU (the rolling RI approach). Approximately 12 months were eliminated from the baseline schedule in this manner. The FFA parties have all informally agreed to the new Revision I schedule and the Army is committed to achieving it. The May 1991 Revision I schedule coincides with the congressionally mandated schedule to complete the RI/FS document in three years. Highlights of the accelerated of Revision I schedule are shown on the schedule comparison table below.

Further acceleration will be realized if the acceleration measures within this plan are implemented. This Revision II accelerated schedule is shown on the comparison table below and graphically on Plate 2.

SCHEDULE COMPARISON

Draft Final RI/FS	Final RI/FS	Final Proposed Plan	Final ROD	Start Remedial Action	Complete Remedial Action	
1. 15 Nov 95	15 Dec 95	15 Jun 96	1 Mar 97	15 Feb 00	15 Sep 03	
2. 15 Nov 94	15 Dec 94	15 Jun 95	1 Mar 96	15 Feb 99	15 Sep 02	
3. 15 Sep 94	15 Oct 94	15 Sep 94	1 Mar 95	1 Jul 95	30 Aug 98	

Utilizing the acceleration measures presented in this acceleration plan, Fort Ord believes the schedule can be reduced 30 percent to 40 percent over the original FFA baseline schedule.



^{1.} November 1990 FFA schedule

^{2.} May 1991 Revision I schedule

^{3.} Revision II schedule

This acceleration will allow most currently contaminated property at Fort Ord to be available for possible real estate transactions in the 1998 time frame- a schedule reduction of at least five years.

SUMMARY

This plan for acceleration of the cleanup of Fort Ord incorporates the efforts of the Fort Ord Team with input from the regulatory agencies that are part of the FFA. Elements of this plan are most likely applicable to other federal facilities throughout the country that have BRAC or NPL objectives. Although not all of these concepts may be applicable, the authors have found through experience that effective communication with regulatory agency personnel provides the greatest avenue for incorporating these and other acceleration measures.

REMOVAL OF A WORLD WAR I ERA WAR GAS FROM A SITE LOCATED IN CLOSE PROXIMITY TO MILITARY DEPENDENT HOUSING AND MILITARY/CIVILIAN WORKERS

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ALPHA BROMOBENZYL CYANIDE (BBC)

A comprehensive plan was needed to transfer the contents of a buried vessel containing alpha-bromobenzyl cyanide (BBC) aka bromophenylacetonitrile (a World War I vintage lachrymator). The primary health and safety concerns associated with this action would be chemical exposure from the BBC or its decomposition products and the physical effort involved in handling the equipment and materials to perform the removal.

The purpose and need for this removal was to mitigate the potential threat to human health and the environment resulting from the presence of 500 gallons of BBC from a buried container which had surfaced adjacent to work areas and on post military dependent housing. The buried vessel is in an area known as the 103 dump site where historical data refers to the burial of wastes, ordnance, and demolition debris from a World War I vintage mustard oil plant in the area.

Due to the chemicals present and the risk of formation of potentially toxic by-products (ie, hydrogen cyanide), the removal required extensive planning, temporary evacuations, site control, and the construction of a emissions reduction unit with one absorption and two adsorption media devices. The emissions reduction unit was installed prior to performing liquid transfer to reduce the amount of organic vapors, hydrogen cyanide, and other gases that may be released. These precautions were needed since occupied on post housing is 2400 feet away and the closest off post housing is 7000 feet away. In addition, military and civilian workers' activity and workplace locations are located within 8000 feet of the site.

A description of the important design parameters of the emissions reduction unit for successful implementation is presented. Also, a description is provided of the public involvement process required to be implemented. This process hand to encompass both on and off post residents along with military and civilian workers.

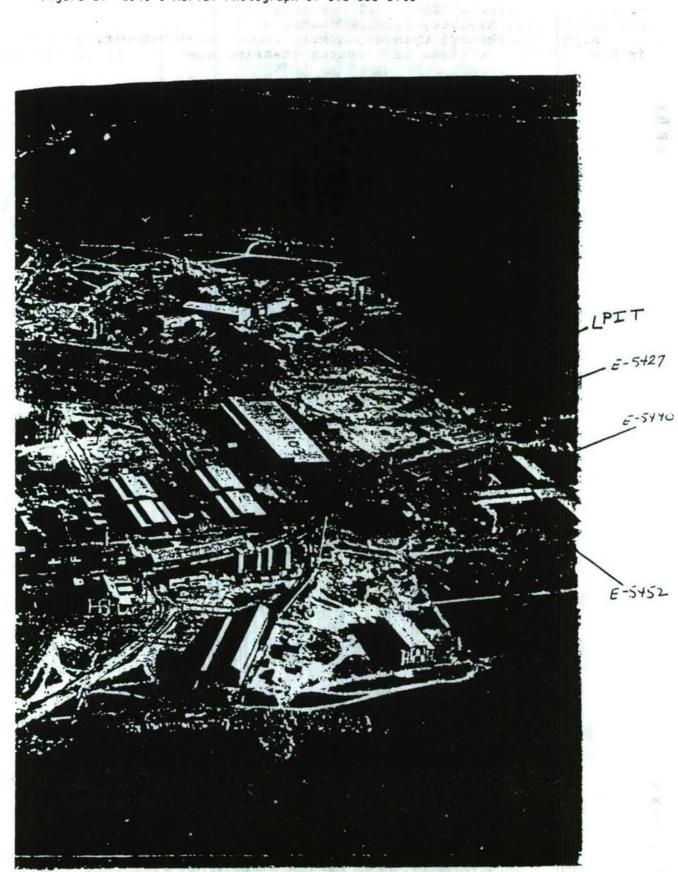
INTRODUCTION/SITE DESCRIPTION

This project provided for the mitigation of a potential health and environmental threat presented by an estimated 500 gallons of alpha bromobenzyl cyanide in an underground vessel at Aberdeen Proving Ground (APG). The vessel is located near Building E5422 in the Edgewood Area of APG, referred to as Building 103 Dump. (See Figure 1)

The RCRA Facility Assessment of the Edgewood Area, Aberdeen Proving Ground had identified this vessel due to its exposure as a result of soil erosion in this area. Interim remedial actions of removing and disposing of the vessel's contents without disturbing the vessel was the chosen course of action. Continuing RFI work is addressing whether Building 103 Dump is a source of ground-water contamination. If the site is not a continuing source, long term control of the site and monitoring of the ground water may be



Figure 1: 1940's Aerial Photograph of Old 103 Site



preferable to cleanup of the site because of the possible hazards

associated with military agent/ordnance dumps.

Alpha Bromobenzyl Cyanide, a.k.a. bromophenylacetonitrile, (CA), is a World War I vintage lachrymator (tearing agent). The industrial preparation consists of chlorinating toluene to form benzyl chloride. The benzyl chloride is then converted to benzyl cyanide by the action of sodium cyanide in an alcoholic solution. Finally, CA is formed via the bromination of the benzyl cyanide. This final reaction utilizes bromine vapors in dry air and initially requires the use of a catalyst to start the reaction; either ultra violet light or sunlight can be used. CA is soluble in organic solvents, alcohol, acetone, and slightly soluble in water. At room temperature it is a flowable, oily liquid, heavier than water, with the odor of sour fruit (odor threshold is approximately 10 ppb).

CA was initially developed by the French in 1918 for riot control

CA was initially developed by the French in 1918 for riot control and subsequently introduced into Germany and the United States. At the Edgewood Area, approximately 20,000 pounds of CA was produced experimentally at Building 601 in 1920. Although CA proved to be a superior lachrymator, its low volatility limited its tactical uses. Subsequent to this, CA wa never produced in large quantities. It is now referred to in the literature as an obsolete military chemical

warfare agent.

Indoor releases of this chemical can result in lethal dosages. The median incapacitation dosage is approximately 30 mg-min/m3, while the lethal concentration is believed to be 900 mg per cubic meter for 30 minutes. Tearing will occur immediately at 0.3 mg per cubic meter (0.0003 mg/L for 3 minutes). It principally affects the mucus membranes, although it can irritate the skin upon contact. Because the material had been in storage for approximately 30 to 50 years, it was expected that decomposition products would present additional health concerns.

BACKGROUND

The area known as the Building 103 Dump is a former waste dumping and burial site. It was originally a sand pit used during WWI when the chemical and filling plants were constructed at APG-EA. After WWI, the sand pit became a dump site for miscellaneous wastes including junk and possibly chemicals. The site was used for waste disposal until the late 1930's or early 1940's. (See Figure 1)

The dump area is approximately 320 feet from north to south, 280 feet from east to west, and occupies an area of about 1.7 acres.

The only reference to the Building 103 Dump is in a document or "diary" on Edgewood Arsenal, 1946, in which there is a report of agent filling of munitions at this location. Interview information is limited; however, one person remembers that the use of the pit included disposal of three mustard gas storage containers, still containing some mustard and sulfur sludge, and that some ordnance may have also been disposed. There is almost no information available concerning the amount of chemical waste placed into the Building 103 Dump. It is possible that the unit was used mainly for disposal of unserviceable equipment and vehicles at that time. It remained in use as a dump site until 1944.

The vessel containing the CA and its decomposition products is constructed of steel and is lead-lined due to the reactivity of CA



with most metals. It is suspected that CA could react violently with iron due to its bromine content. The vessel's capacity was estimated to be 5,000 gallons and it was original estimated that the total volume of the CA and decomposition products to be 500 gallons. The vessel is positioned horizontally and is slightly exposed above the ground surface. Due to the age and unknown condition of the container and the surrounding subsurface area, it was determined that the interim remedial actions would be based on minimal disturbance to the site to avoid the potential for release. An Environmental Assessment (EA) was written and approved by 12 December 1991. A public meeting was held on 09 January 1992 explaining the details of project.

The vessel was originally noticed surfacing from the landfill in 1989. (See Figure 1-2) The U.S. Army Chemical Research, Development, and Engineering Center (CRDEC) collected a sample to determine whether the vessel contained mustard or other surety materials. Results

showed that the following constituents were present:

alpha-bromobenzyl cyanide
1,2-dicyano 1,2-diphenylethane
benzaldehyde
benzoic acid
phenylacetic acid
benzyl cyanide

(See Figure 1-3 for the chemical structure of the compound)

CONSIDERATIONS

Vessel is located near family housing area. (See Figure 1-4) An active industrial work zone would have to be evacuated. Main streets would have to be closed and barricaded.

Work time would have to be coordinated with U.S. Army medical personnel as there was a potential for release of military agents.

Since after normal duty hours (8am-4:30pm) were selected for the operation artificial lighting had to be provided.

Communications had to be established between military units (Military Police, Technical Escort Unit) and civilian contractors (Weston, Chemical Waste Management, Human Factors Applications).

Weather (High winds, rain, sleet, snow were all seasonable)
In fact due to high winds the project was delayed
from March 17th to March 18th. Work was performed
during a mixture of rain, sleet and snow.

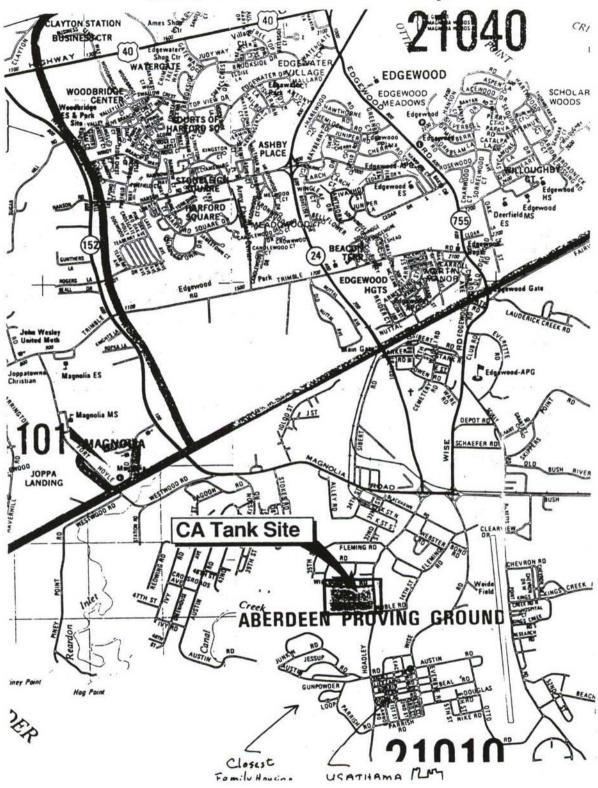
TECHNICAL APPROACH

A sequential approach was developed for the implementation of the remediation activities to be performed at this site. The technical approach consisted of the following activities:

WILLIAMS ROAD EXPOSED AREA FIGURE 1.2: CA VESSEL IN BLUIDING 103 DUMP (NOT TO SCALE)

3 STRUCTURE OF CA Z Ⅲ ○

BBC Removal Site Map



Development of Work Plan and Environmental Assessment. Perform UXO Sweep.

Implement site controls for sampling.

Sample contents of vessel.

Characterize contents of vessel.

Analyze disposal alternatives/select transporter and disposal facility.

Take sample of vessel contents for disposal facility.

Mobilize for remedial activities.

Transfer vessel contents to poly-drum containers.

Obtain wipe sample of vessel (and nonpumpable residuals if present).

Transport containers to treatment/disposal facility. Post-remediation activities (stabilization) for the vessel.

Prepare final reports (including certifications).

MOBILIZATION

In February 1992, after development of work and safety plans, staging was performed at the site to retrieve a sample and measure the vessel. This sample was required to further characterize the waste to determine which treatment/disposal facility would be chosen for destruction/disposal. An EOD Subcontractor performed the surface sweep clearance and the actual excavation of the vessel. Excavations were limited to only approximately six inches of overburden which was removed with the sides and ends outlined to facilitate volume measurements. While excavations were being conducted the Army's Technical Escort Unit personnel were monitoring for the potential release of military chemical agents. This was necessary since it is strongly suspected that mustard gas and mustard by-products were disposed of in the pit. Contractor personnel were also performing air monitoring using OVA, CGI/O2 meter, monitox and Drager Tubes. Work was performed after normal duty hours with the area adjacent (within 650 feet) evaluated and blocked. (See Figure 1-5)

The container was access using a high speed, bi-metal, hole saw, cutting a minimum of a 4.5 inch diameter hole in the center of the prepared area. A continuous flow of water soluble cutting fluid was sprayed on the hole saw during the cutting operation. Personnel performing this operation were in EPA Level B personal protective

equipment. This consisted of:

Supplied-air respirator.

One piece Saranex whole body coverall.

Gloves (outer), chemical-resistant, Nitrile.

Gloves (inner, chemical-resistant (latex).

Leather Safety boots/shoes with chemicalresistant soles, steel toes and shanks with
boot covers (outer), chemical-resistant
(disposable).

Chemically protective safety boot (Beta Polymax or equal) as an alternative to the leather boot with cover.

Hard hat.



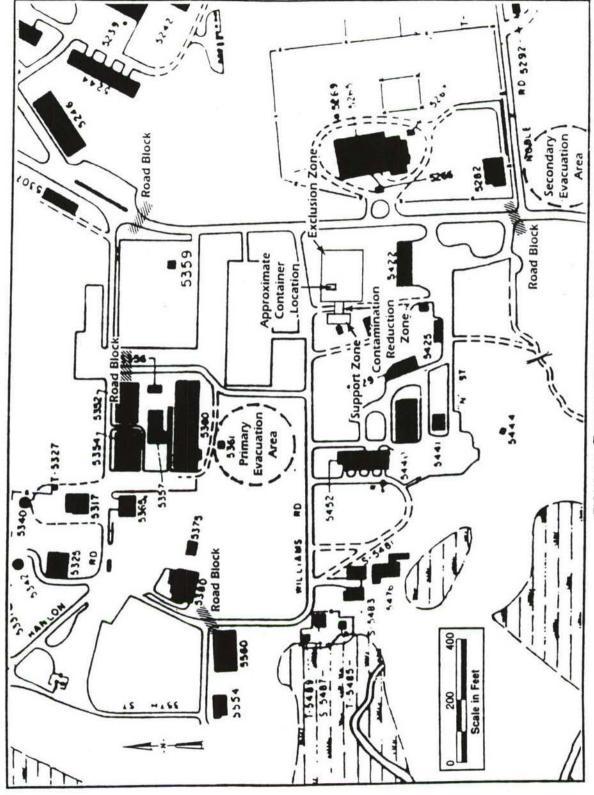


FIGURE 1-5 SITE WORK ZONE MAP

Splash shields for use during high splash hazard activities.

The vessel was access and a 64 ounce teflon sample jar was filled by using a 25 gpm knynar teflon pump. Internal and external measurements of the vessel were conducted at this time. Upon completion of measurements and packaging of sample jar the vessel was resealed with a teflon coated steel plug, removed overburden was replaced over the vessel.

Based on the analysis of the sample (see Table 6-2), Chemical Waste Management, located in Port Arthur, Texas, was chosen as the disposal facility, with incineration as the method of disposal.

The prime contractor fielded a project team in March 1992 to execute the removal and subsequent containerizing of the CA waste. The site crew consisted of a Field Operations Manager (FOM), a Site Safety and Health Officer (SSHO), a Site Engineer (SE), and Field Technicians (FTs), with a maximum crew of nine.

AIRBORNE DISCHARGE CONTROL MEASURES

Due to the chemicals present (i.e., alpha bromobenzyl cyanide) and the risk of formation of potentially toxic by-products (i.e., hydrogen cyanide (HCN) and ammonia (NH3)), with respect to the proximity to civilian housing and civilian/military workforce, an Emissions Reduction Unit (ERU), was designed and constructed over the CA vessel prior to performing liquid transferral and container rinsing activities to reduce the amount of organic vapors, HCN, and NH3 gases that may be released. ERU schematic is shown in Figure 2-1. The unit consisted of the following:

Poly shelter, constructed of polyethylene and PVC piping or wood two by fours.

Two 60cfm (max) blowers.

Two drums of granular activated carbon (GAC) (150 pounds each).

55-gallon container, for aqueous caustic (NaOH) solution, in case of spills.

50 lbs of whetlerite carbon unit (carbon impregnated with copper and hexavalent chromium).

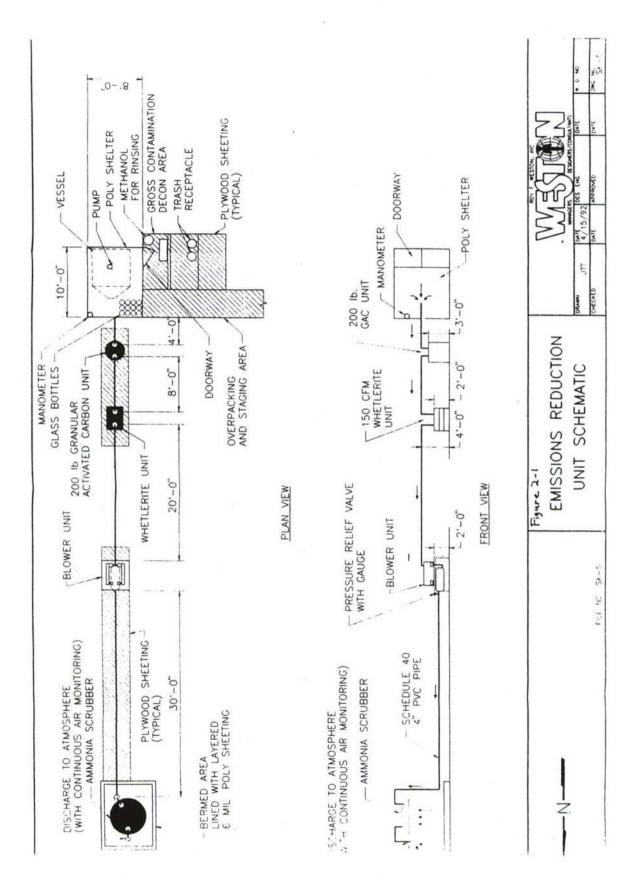
1,000-gallon poly tank to be used as an ammonia absorber (containing 750 gallons of a 15% NaOCl solution).

Various 4" and 2" PVC pipe for system plumbing.

Manometer, to measure the pressure difference between the inside of the poly shelter and the outside atmosphere.

(A negative pressure was maintained inside the poly shelter to prevent the possible release of toxic vapors)

As shown in Figure 2-1, the ERU uses two adsorption media and one absorption device to reduce vapor emissions. The initial medium used will be granular activated carbon (GAC). GAC was chosen for its adsorptive capabilities on a wide variety or organic compounds. In this case, it is being used to adsorb alpha bromobenzyl cyanide. Although, there is currently no isotherm data available for the adsorption of alpha bromobenzyl cyanide onto GAC, its low vapor pressure (0.267mm Hg at 60 degrees C) and high molecular weight (196





grams/g-mole) should allow it to readily adsorb onto GAC. Vapor-phase adsorption of a compound is a condensation process of the compound onto the carbon. The lower the vapor pressure and the larger the molecular weight, the more readily a compound should condense onto the carbon. Also, vapor emissions of CA are expected to very low due to

its high vapor density (six times greater than air).

The second medium chosen, a whetlerite carbon, will be used to capture and neutralize any HCN gases released. Whetlerite carbon is a carbon that has been impregnated with various metals, in this case copper and hexavalent chromium, to enhance the adsorption capacity of activated carbon. This product is currently used in military personnel protective equipment and also in industry for the capture of acid gases. The primary mechanism for adsorption in this case is via a chemical reaction between the impregnated metals and the HCN. This phenomenon is known as chemisorption. HCN in the presence of copper (Cu +2) tends to be oxidized to form cyanogen (CN)2. Cyanogen is then hydrated through a reaction with chromium (Cr +6) to form oxamide (CONH2) that remains adsorbed onto the carbon. Although the exact mechanism of hydration remains uncertain, chemical analyses demonstrate that oxamide is formed.

The amount of whetlerite carbon required was determined based on a traumatic release during rinsing of the vessel, which would be the release of all the CN associated with 10 percent of the original 500 gallons. This amount (10 percent of volume) was assumed to be nonpumpable material, which was confirmed during sampling. The amount of HCN that could potentially be released, 83.5 pounds, the whetlerite HCN breakthrough testing data (provided by the Chemical Research Development, and Engineering Center (CRDEC), and air emissions standards from COMAR 26.11.15 for Class II Toxic Air Pollutants at an 8-hour screening level (a maximum 7.5 mg pollutant/m3 air at the emissions point or 0.05 mg pollutant/m3 air at nearest living quarters were used to determine whetlerite carbon requirements for the ERU. CRDEC data provided a 6.35 percent by weight adsorption (63.5 mg HCN/g carbon). The amount of carbon required was then determined to be approximately 1,315 pounds. However, a safety factor of two was used to ensure capture of the potentially released HCN gas. Two whetlerite carbon units (containing 1,440 pounds of carbon each), was used. These units have been designed to handle a maximum flowrate of 5,000 The maximum flow of the ERU system will be 60 CFM, thus providing for a more than adequate contact time for the chemisorption. This lower flow through the units will increase the contacting time by 83 times.

An absorber was used to remove any NH3 that may have been produced during rinsing of the vessel. It was estimated that approximately 33 pounds could be released; however, the system was designed to handle up to 81 pounds. Also, a gas flow of 60 CFM should allow for an adequate contacting time.

Therefore based on the amount of activated and whetlerite carbon used, the design of the ammonia absorber, and the contacting time provided, all the CA, HCN, and NH3 should be removed. However, emissions monitoring (ammonia, HCN, and organic vapors) was performed continuously at the vent to atmosphere of the ERU. If the emissions exceed the COMAR standards, the air flow through the ERU would be reduced to increase contact time.

Once the contamination control measures were in place the vessel was accessed by removing the overburden and the teflon coated steel

plug. All work to remove the liquid was performed in the poly shelter with personnel in Level B protection. The liquid was transferred from the container to 64 ounce teflon sealed glass jars and overpacked into fiber board containers. (size of containers were dictated by the disposal facility and the estimated amount of the liquid in the vessel had been greatly reduced from subsequent measurements taken when the vessel was accessed for the February sample) Again, the liquid was removed via a kynar/Teflon constructed pump. The overpacked containers were transferred to from the exclusion zone to the support zone and loaded for truck shipment by Chemical Waste Management personnel.

During all site activities continuous air monitoring was being performed by using the OVA, CGI/O2 meter, monitox, and Drager Tubes. Monitoring was being conducted both inside the ERU and at the ERU

discharge point.

Following removal of the liquid, the container was rinsed with methanol. Methanol was selected because it demonstrated much greater miscibility with the liquid in the vessel, with no off-gas or heat generation, and no solids precipitation. Again the rinsing operation was performed inside of the poly-shelter and in Level B protection to reduce the risk of exposure. Rinsate generated was pumped into overpacked poly-drums and packaged with the containerized waste. Following the transfer of liquid rinsate, a wipe sample of the container wall and a sample of any residue was collected with personnel in Level B protection. (A 3" by 3" methanol wetted sterile gauze was used to collect the sample) The sample was taken to document the remaining bromine and cyanide concentrations and to identify the conditions in which the container was to be left at the end of this interim remedial activity. (Results are shown in Table 6-2)

POST-REMEDIATION

Post-remediation activities of the vessel included the placement of 50 pounds of granular activated carbon into the vessel to adsorb any organic compounds that may volatilize, and the capping of all openings with nonmetallic fittings. Since the container is to remain in place, all excavated soil was replaced. Clean soil was imported and placed over the originally excavated soil. The poly shelter was removed and concrete barriers were placed over the container to act as ballast and as a barricade.

SUMMARY OF PROJECT SAFETY PROCEDURES

SITE-SPECIFIC TRAINING - Field personnel were trained during each phase of work to prepare for the specific hazards of those activities. Training was given prior to sampling activities and liquid removal activities. Items covered included the scope of activities, the responsibilities of site personnel, specific site hazards, PPE, monitoring, decontamination, and emergency response. As part of training, the EOD subcontractor, Human Factors Applications, Inc.(HFA), conducted a briefing to familiarize personnel with UXO (Unexploded Ordnance) hazards and procedures. Field personnel were also required to review the SHERP (Safety, Health, and Emergency Response Plan), and certify that they understood and would comply with the requirements set forth by the SHERP.



Table 6-2

Summary of Analytical Results

Parameter	Results				
% Bromide	23.68				
% Cyanide (total)	1690000 above reporting limiting ug/l				
Ignitibility	No flash point observed				
TOC	LOI				
% Ash	LOI				
Loss of ignition	100%				
Viscosity	30.5 CP				
Heat of Combustion	9230 Btu/lb				
TCLP (Lead)	ND				
Reactivity - Cyanide	ND				
Reactivity - Sulfide	ND				
pН	4				
Wipe Sample Bromine	6.28 mg/cm ² €				
Wipe Sample Cyanide	0.07 mg/cm ²				

N.D. = Not Detected

LOI = Loss of Ignition

CP = Centi Poise

F.P. = Flash Point

UG = Micro gram

BTU/LB = British Thermal Unit per pound

* Unit for wipe sample results are for milligram per unit area.

AIR MONITORING - The objectives of the air monitoring program for this project were as follows: (1) to determine the action levels for PPE; and (2) to monitor for the potential release of ammonia, organic vapors and cyanide vapors to the environment.

PERSONAL PROTECTION/ENVIRONMENTAL MONITORING - Personal protection air monitoring was conducted with a Foxboro OVA, a HCN Monotox meter, and Calorimetric tubes. Action levels from all instruments were specified in the SHERP. A record of all monitoring activity was maintained and attached to the daily safety reports. The activities monitored included: hand excavation, vessel accessing, sampling, transfer of vessel contents and rinsing of the vessel. The following summarizes the air monitoring equipment and its use:

EQUIPMENT
ICAD
CAM
OVA (FID)
HNu (PID)
Calorimetric Tubes
HCN Monotox
CGI/O2 Meter
Micro R Meter

MONITORING USE
Chemical Surety Material
Chemical Surety Material
Organic Vapors
Organic Vapors
Benzene/Ammonia
Hydrogen Cyanide
Explosive Limit/Oxygen Level
Gamma Radiation Hazard

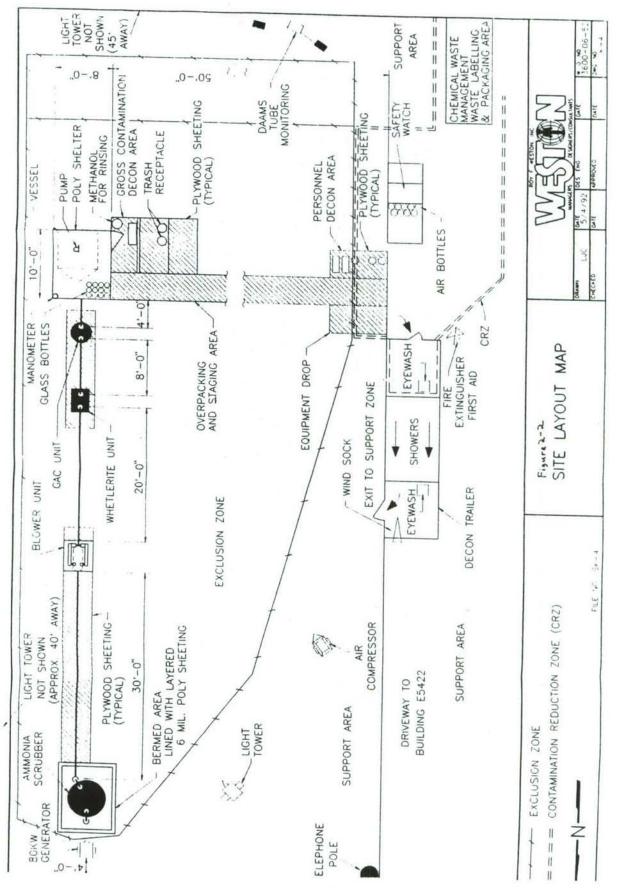
During hand excavation activities U.S. Army Technical Escort Unit (TEU) provided two technicians to perform chemical agent monitoring with CAMs. HFA personnel performing the hand excavation wore ICADs for personal chemical agent monitoring. Both the ICAD and CAM are real time monitoring devices which monitor at or above the IDLH level for most Chemical Surety Material (CSM). Chemical agents were not detected by either the CAM or ICAD. Also, an OVA was used during hand excavation. The OVA was placed adjacent to the excavation and left in the monitoring mode. At no time did the alarm sound or were action levels exceeded.

Monitoring during the drilling and sampling activities included the OVA, HCN Monotox, Micro R Meter, the CGI/O2 meter. Monitoring readings were recorded approximately every 15 minutes during the 2 1/2 hour period from the start of drilling to retrieving a sample from the vessel. When the vessel was initially opened the OVA recorded a reading of 1.5 units above background, however this was below the stop work action level. The CGI/O2 measured no explosive hazards at the mouth of the vessel, the HCN Monitox measured no HCN vapors present and Micro Meter detected nothing above background. No readings from monitoring instruments exceeded stop work action levels.

In addition, during the sampling phase and later during the liquid removal phase, low volume air sampling pumps were used for low level CSM air monitoring. These units were located down wind along the perimeter of the exclusion zone. These low volume air sampling pumps were provided by the CRDEC Chemical Support Division, Monitoring Branch. Absorbent tubes were used as a collection medium, and later analyzed for chemical surety materials, all of which were negative.

During liquid removal activities air monitoring was conducted both inside the poly shelter and at the vent to the atmosphere of the ERU. As presented in Figure 2-1, the poly shelter was set-up over the buried vessel. An OVA, HCN Monotox, CGI, and Calorimetric tubes (for ammonia and benzene) were used for monitoring inside the shelter. At the vent to the atmosphere of the ERU, a HNu (PID), HCN Monotox, and





Calorimetric tubes for ammonia were used to monitor emissions to the atmosphere.

On the initial night (18 March 1992) of removal activities no readings from monitoring instruments exceeded the stop work action level. (Operations were originally scheduled for the March 17 but were cancelled, as a safety precaution, due to high winds) Readings taken inside the poly-shelter did not exceed background readings. Readings at the exhaust to the atmosphere of the ERU did however, include a maximum reading from the HNu to be 38 units and 6 units for the HCN Monotox. The Calorimetric tubes were used to support the HNu at the vent to the atmosphere. No response for ammonia was indicated therefore, work was not stopped. Also, since the monitox inside the shelter did not indicate HCN present and the stop work action level for HCN was 10 units the work proceeded without stoppage. Work was stopped but it was due to failure of the pump to carry the liquid through its tubing. (Heavy viscosity of the liquid resulted in tubing collapse)

On the second night (19 March 1992) of liquid removal activities, readings above the stop action level were detected from the HNu at the exhaust at the atmosphere of the ERU. At approximately 6:15 pm, a reading of 1100 units was recorded. This reading was sustained continuously for approximately one minute. At that time work was stopped and the vessel sealed. At the same time, readings from instruments inside the poly-shelter had not exceeded the stop work action levels. The HNu was taken inside the shelter and monitored. Although the readings were slightly elevated (30 units), they did not exceed the stop work action level of 50 units. The vessel was reopened and work was continued. Only one other reading from the HNu was detected above the stop work action level. This took place at approximately 7:40 pm. The reading was approximately 63 units, however this reading was not sustained. It was determined based on the readings inside the shelter that the reading of 1100 units may have been due to interference from moisture or mists from the ammonia scrubber, or

possibly exhaust fumes of the diesel generator on-site. The location of the exhaust of the generator and a change in wind direction may have caused the elevated readings. A HNu will respond to diesel exhaust fumes. The Calorimetric tubes for benzene and ammonia detected no concentration of either compound. The HCN Monotox did not exceed stop work action levels at the exhaust to the ERU.

Inside the poly shelter none of the instruments indicated readings above the stop work level. Prior to rinsing the vessel with methanol the vessel was purged with nitrogen to 6% 02 level.

CONCLUSION

In the past, for remediation projects two safety philosophies have been used for coping with inevitable uncertainties; 1) either to adopt excessive factors of safety; 2) or else make assumptions based on general average experience. The first method is wasteful, the second is dangerous. A third method as described in the present paper is based on experimental methods or "learn as you go". This "learn as you go" method allows for corrections and modifications to be made on a basic plan once actual field and laboratory data, and actual field experience has been accumulated.

NOAA Response Information Data Base

NOAA - 7600 SAND POINT WAY NE SEATTLE, WA 98115 (206) 526-6317 CHEMTREC (800) 424-9300 OR (202) 483-7616

Chemical Name: BROMOBENZYL CYANIDE

Synonyms:

2-BROMO-2-PHENYLACETONITRILE ACETIC ACID, BROMOPHENYL-, NITRILE ACETONITRILE, BROMOPHENYL-ALPHA-BROMBENZYLKYANID (CZECH) ALPHA-BROMO-ALPHA-TOLUNITRILE ALPHA-BROMOBENZENEACETONITRILE ALPHA-BROMOBENZYL CYANIDE ALPHA-BROMOBENZYLNITRILE

ALPHA-BROMOPHENYLACETONITRILE BBC

BBN

BENZENEACETONITRILE, ALPHA-BROMO-BENZENEACETONITRILE, ALPHA-BROMO- (9CI)

BROMBENZYL CYANIDE

BROMOBENZYL CYANIDE

BROMOBENZYL CYANIDE (DOT)

BROMOBENZYLNITRILF

CA

CAMITE

UN Number: 1694

RTECS: AL8050000

STCC:

4925210

Formula: C8H6BrN

CAS Number: 5798798

Label:

Portions @ CAS, 1987

knock-down vapors. (@AAR, 1990)

Protective Clothing:

These protective clothing recommendations are based on the chemical classification "Cyanides" from Guidelines for the Selection of Chemical Protective Clothing, 3rd edition, 1987.

Neoprene: Good Resistance / Limited Data (A.D. Little, 1987)

First Aid:

Move victim to fresh air and call emergency medical care; if not breathing, give artificial respiration; if breathing is difficult, give oxygen. In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes. Remove and isolate contaminated clothing and shoes at the site. Effects should disappear after individual has been exposed to fresh air for approximately 10 minutes. (DOT,1990)

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MIGRATION OF NITROAROMATIC COMPOUNDS IN UNSATURATED SOIL AT THE ABANDONED WELDON SPRING ORDNANCE WORKS, ST. CHARLES COUNTY, MISSOURI

John G. Schumacher¹, Chris E. Lindley², and Forrest S. Anderson²

ABSTRACT

Studies are being conducted at the abandoned Weldon Spring Ordnance Works in St. Charles County, Missouri, to determine the potential for migration of 2,4,6-trinitrotoluene (TNT) and other nitroaromatic compounds from contaminated surficial soils into the shallow bedrock aquifer. Unconsolidated materials at the site range from 0 to more than 61 feet thick and consist of topsoil or fill, modified loess, glacial drift, and residuum. The U.S. Army has detected concentrations of TNT ranging from less than 1 mg/kg (milligram per kilogram) to more than 81,000 mg/kg in more than 5,700 surficial soil screening samples from the 1,655-acre site. Concentrations in the soil decreased rapidly with depth. In 21 of 24 soil borings with surface TNT concentrations larger than 1,000 mg/kg, concentrations decreased to less than 10 mg/kg at depths of 3 to 4 feet.

The U.S. Army also has detected small concentrations of TNT ranging from less than 0.15 µg/L (microgram per liter) to 19 µg/L, dinitrotoluene (DNT) ranging from less than 0.1 µg/L to 8.5 µg/L, and small quantities of 1,3,5-trinitrobenzene (TNB) and nitrotoluene in water samples from 12 of 34 monitoring wells at the site. Several lysimeters were installed in the shallow unsaturated zone at the site to determine if migration from contaminated surficial soils could be a source of the nitroaromatic compounds detected in the ground water. Concentrations of TNT in surficial soil samples above the lysimeters ranged from 120 mg/kg to more than 31,000 mg/kg. Concentrations of TNT were detected in 18 of 23 subsurface core samples collected during lysimeter installation; however, the concentrations generally decreased to less than 2 percent of the surface concentrations at depths below 2 feet. One of the 23 soil core samples had a small (0.30 mg/kg) concentration of 4-amino-2,6-dinitrotoluene (4-Am) and 5 of the soil core samples had detectable (0.34 to 9.11 mg/kg) concentrations of 2-amino-4,6-dinitrotoluene (2-Am). Concentrations of TNB were detected (0.21 to 46.2 mg/kg) in eight soil core samples. Concentrations of total organic carbon (TOC) decreased from an average of 0.17 percent (by weight) in near surface soil samples to less than 0.05 percent in samples below 1.5 feet.

Although TNT concentrations decreased rapidly in the soil within a few feet of the land surface, water samples collected from lysimeters at depths between 1.0 and 3.6 feet contained large concentrations of TNT (4.1 to 6,250 μ g/L), 4-Am (less than 3.0 to 1,740 μ g/L), and 2-Am (5.9 to 246 μ g/L). Concentrations of TNB ranging from less than 3.0 μ g/L to 1,130 μ g/L also were detected in the lysimeter samples. The data indicate decomposition of TNT to 4-Am and 2-Am within the upper (unsaturated) soil and photolysis of TNT to TNB at the surface and subsequent transport of TNB within the soil. The relatively large concentrations of TNT, 4-Am, 2-Am, and TNB in water samples compared to soil core samples indicate these compounds are only weakly sorbed to the low-organic carbon soils at the site and that the measurement of TNT and its degradation products in the soil, by itself, is not adequate to describe the migration of these compounds in the unsaturated zone. The apparent weak sorption of these compounds to the soil and presence of fractures within the overburden at the site indicate these compounds are likely to migrate through the deeper unsaturated zone to the shallow bedrock aquifer at the site.

Seasonal variations in the aqueous concentrations of TNT and 4-Am in the unsaturated zone were detected. These seasonal variations in concentrations probably are related to the initial flushing of the compounds by increased infiltration in the early winter and subsequent dilution of their concentrations by sustained quantities of increased infiltration during the winter. The variation in concentrations may be attributed to increased available soil moisture caused by decreased evapotranspiration. The seasonal variations in concentrations seem to have little "lag-effect," indicating migration within the upper unsaturated zone at this site may be rapid (on the order of a few weeks); however, additional data are needed to confirm this hypothesis.

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INTRODUCTION

Several studies have investigated the microbial, physical, and photolytic degradation and sorption of 2,4,6trinitrotoluene (TNT) in the laboratory setting, including those by McCormick and others (1976), Won and others (1974), Spanggord and others (1980), Spanggord and others (1982), Kearney and others (1983), Folsom and others (1988), Cataldo and others (1989), Pennington and Patrick (1990), and Spanggord and others (1991). investigators have found that 4-amino-2,6-dinitrotoluene (4-Am) and 2-amino-4,6-dinitrotoluene (2-Am) are among the more common degradation products produced by microbial detoxification of TNT in amended soils. Burlinson (1980) indicated that 1,3,5-trinitrobenzene (TNB) was the primary product formed by the photolysis of TNT. Spanggord and others (1980) concluded that experimentally derived soil sorption coefficients for both TNT and 2,4dinitrotoluene (2,4-DNT) were small, which indicated that, compared to photolysis, sorption is not a significant process in attenuation of these compounds from an aqueous environment. Cataldo and others (1989) reported that between 30 and 50 percent of TNT amended to soils was irreversibly sorbed (not removed by subsequent exhaustive extraction) after 60 days. They determined that much of the irreversible sorption was nonbiotic in nature and that nonbiotic transformation of TNT also may be important. Pennington and Patrick (1990) experimentally determined an average sorption coefficient for TNT of about 4.0. Although numerous laboratory studies have examined the chemical, physical, and microbial degradation processes of TNT, little data have been collected in the field to verify the results of laboratory studies. This paper presents results of a preliminary investigation of TNT and other nitroaromatic compounds in soil and water in the shallow unsaturated zone at an abandoned ordnance works facility. These data were collected as part of a larger cooperative effort between the U.S. Army Corps of Engineers and the U.S. Geological Survey to determine the environmental fate of TNT and its potential to migrate through the unsaturated zone to the shallow bedrock aquifer.

HISTORY OF THE SITE

The Weldon Spring Training Area (WSTA) consists of 1,655 acres of land owned by the U.S. Army in south-central St. Charles County, Missouri (fig.1). The WSTA is part of a larger (about 17,000 acres) site formerly owned by the U.S. Army known as the Weldon Spring Ordnance Works (WSOW). The WSOW produced more than 700 million pounds of TNT and smaller quantities of dinitrotoluene (DNT) during its operation between 1941 and 1945. The plant consisted of 18 nearly identical TNT production plants (lines), 2 DNT production lines, and numerous other production support plants, such as nitric acid plants, sulfuric acid plants, ammonia oxidation plants, and other facilities. At peak production the plant employed about 3,000 workers (International Technology Corporation, 1989a) and produced nearly 1 million pounds of TNT each day. Fifteen of the TNT lines, both DNT lines, and nearly all of the major production support facilities were within the boundary of the WSTA site. The remaining three TNT lines were on a 217-acre tract immediately east of the WSTA site now owned by the U.S. Department of Energy. These lines were demolished in 1955 during the construction of a U.S. Department of Energy Uranium Feed Materials plant. An aerial photograph of the WSOW site taken in February 1945 showing the TNT and DNT production lines, production support facilities (southern part of the WSTA), and magazine area (north of the WSTA) is shown in figure 2.

TNT was manufactured at the site by a three stage batch process using toluene, nitric acid, and sulfuric acid as the main raw materials. The purification of impure TNT was accomplished by rinsing the impure TNT with a solution of sodium bicarbonate and sellite (Na₂SO₃) at the "wash-house" complex. This removed isomers other than 2,4,6-TNT and neutralized any remaining acid present. During this process the color of the liquid became red and large quantities of wastes called "red water" that contained various mixtures of water, inorganic salts, ash, sulfonate derivatives, and nitroaromatic compounds were generated (International Technology Corporation, 1989a).

Before mid-1942, the red water was discharged to settling lagoons at WSOW (some of which are visible in figure 2). Contamination of area springs and streams was observed shortly after the construction of the settling lagoons (V.C. Fishel and C.C. Williams, U.S. Geological Survey, written commun., 1944). Because of this observed contamination, a large gravity-flow network of underground wooden wastewater pipelines was constructed in mid-1942 to connect the 18 TNT lines to 3 wastewater-treatment plants (Fraser-Brace Engineering Company, written commun., 1951). Several miles of wastewater pipeline were constructed, of which about 61,000 ft (feet) is still in place (International Technology

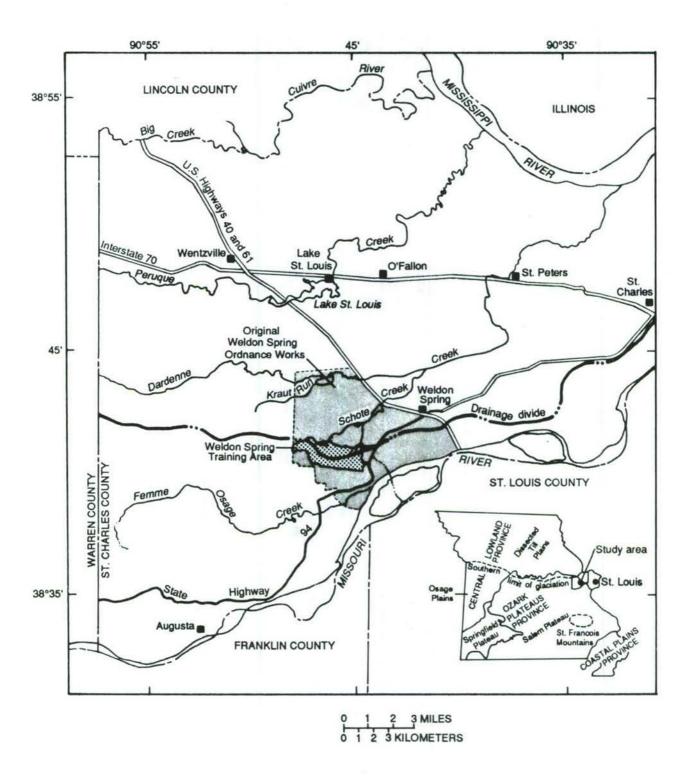
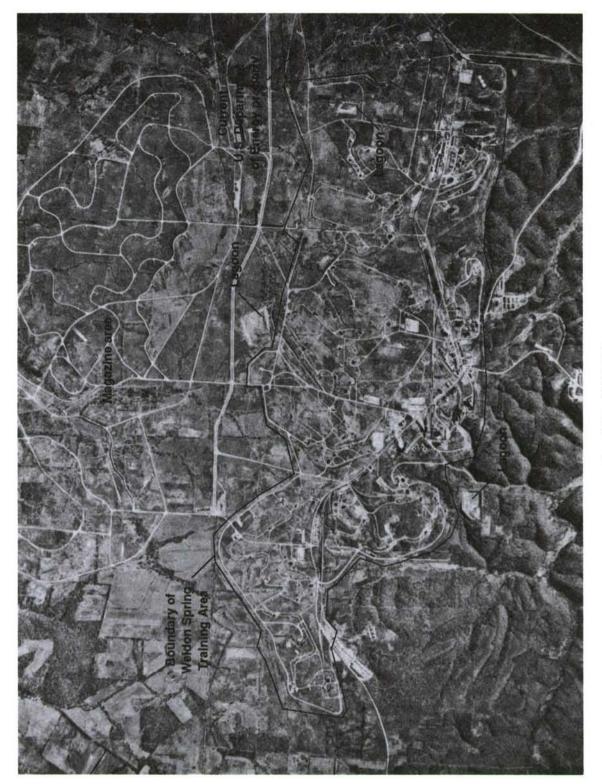


Figure 1.--Location of the Weldon Spring Training Area site and boundary of the original Weldon Spring Ordnance Works (physiography from Fenneman, 1938).



0 1,000 2,000 FEET 0 250 500 METERS

Figure 2.--Aerial photograph of part of the Weldon Spring Ordnance Works production in February 1945 (photograph from U.S. Geological Survey).

Corporation, 1989a). Fishel and Williams (written commun., 1944) indicated the gravity-flow lines often became clogged with particulates, causing the red water to back up and flow directly into gullies and streams on and in the vicinity of the WSTA.

At least four major cleanup operations have been conducted at the site since 1944 (International Technology Corporation, 1989a), leaving only foundations and a few of the more than 1,000 buildings on the WSTA site. Despite these cleanup efforts, concentrations of TNT, ranging from less than 1 mg/kg (milligram per kilogram) to more than 81,000 mg/kg, have been detected in soils around former production buildings (International Technology Corporation, 1989a). Red-stained soils and stressed vegetation are common in these areas. The U.S. Army has analyzed more than 5,700 surficial soil screening samples from fixed grids at the WSTA site (International Technology Corporation, 1989a). These grid areas encompassed all known TNT production and transportation areas at the WSTA site (fig. 3). Within each grid area, surficial soil samples were collected at regular intervals of 40 or 80 ft and screened onsite for TNT concentrations using a procedure developed by the U.S. Army Corps of Engineers (Medary, 1992). Results of the screening tests indicated much of the soil contamination was associated with wash houses and nearby waste-water settling tanks (International Technology Corporation, 1989a). The excessive soil contamination was restricted to isolated areas. Less than 5 percent of the surficial soil samples contained TNT concentrations larger than 1,000 mg/kg and more than 90 percent of the surficial soil samples contained TNT concentrations less than 30 mg/kg. Contamination in the wash house areas probably resulted from spillage of waste liquids containing dissolved and finely particulate TNT. Laboratory analyses of soil samples generally confirmed the screening data for TNT; and detected concentrations of other constituents such as 2,4-DNT and 2,6-dinitrotoluene (2,6-DNT).

Although large concentrations of TNT have been detected in surficial materials at the WSTA site, concentrations generally decreased to less than the detection limit (1 mg/kg) at depths greater than about 5 ft below the land surface (International Technology Corporation, 1989b). More than one hundred 5-ft deep soil cores were collected within the grid areas. Screening tests on samples from 1 ft intervals in these cores indicated large decreases in TNT concentrations with depth. For example, in 21 of 24 cores with surface concentrations greater than 1,000 mg/kg, TNT was detected in only 3 cores at a depth of 4 ft and only 1 core at a depth of 5 ft (International Technology Corporation, 1989b). Analytical tests on 44 samples from these cores indicated no detections of 2,4-DNT or 2,6-DNT. However, TNB was detected in 25 of the samples (depths from 1 to 5 ft) at concentrations ranging from 1 to 280 mg/kg. Neither 4-Am or 2-Am were analyzed in any of the U.S. Army samples.

The U.S. Army has detected small concentrations of TNT ranging from less than $0.15 \,\mu\text{g/L}$ (microgram per liter) to 19 $\mu\text{g/L}$, DNT ranging from less than $0.1 \,\mu\text{g/L}$ to $8.5 \,\mu\text{g/L}$, and smaller quantities of TNB and nitrotoluene in water samples from 12 of the 34 monitoring wells at the site (International Technology Corporation, 1990). Sufficient data have not been collected to determine if the source of this contamination is related to red water disposal practices during production or to leaching of small quantities of TNT and other nitroaromatic compounds from contaminated surficial soils at the WSTA. Consequently, the primary objective of this preliminary investigation was to determine if substantial quantities of TNT and other nitroaromatic compounds are migrating to the ground water from contaminated surficial soils.

DESCRIPTION OF THE WELDON SPRING TRAINING AREA

Since the WSOW was declared surplus property in 1946, the U.S. Army has transferred ownership of all the original WSOW property, except the 1,655-acre WSTA site. The entire site was used for U.S. Army reserve training until 1989 and part of the site was reopened for training activities in 1990. The WSTA is situated along the boundary between the Dissected Till Plains of the Central Lowland Province to the north and the Salem Plateau of the Ozark Plateaus Province (Fenneman, 1938) to the south (fig. 1). The topography of the northern part of the site is characterized by a gently undulating surface of unconsolidated Quaternary loess and glacial drift deposited on residuum and weathered Keokuk and Burlington Limestones of Lower Mississippian age. The topography changes to more rugged, steeply dipping slopes with little glacial drift in the southern part of the site. Average annual precipitation is about 34 in. (inches) per year (National Oceanic and Atmospheric Administration, 1988).

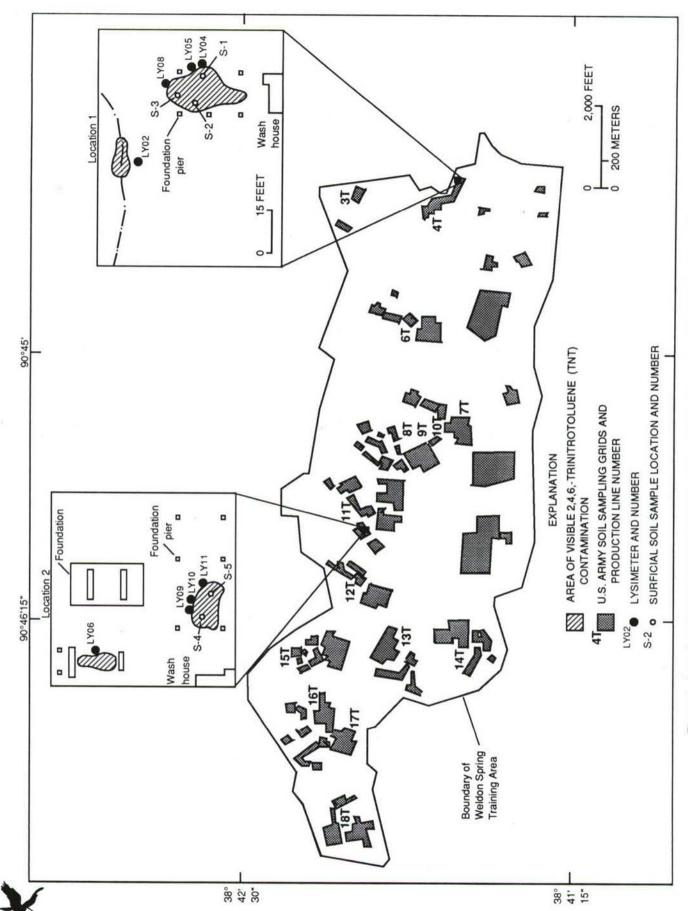


Figure 3.--Location of production line sampling grids and lysimeter nests at the Weldon Spring Training Area.

Much of the WSTA site is underlain by overburden deposits of variable thickness composed of a silty, organic-rich topsoil or fill, modified loess, glacial drift, and residuum. The thickness of these deposits ranges from 0 (in the southern part of the site and within stream channels) to more than 61 ft in the northern part of the site (M.L. Rueff, Missouri Department of Natural Resources, Division of Geology and Land Survey, written commun., 1992). The topsoil generally is less than a few feet thick and is absent in many production areas because of excavation during previous cleanup operations. The modified loess (0 to about 10 ft thick) is a very stiff clayey silt that generally has a low moisture content. Vertical joints have been observed within this unit. The glacial drift (0 to more than 55 ft thick) is composed of clay with variable quantities of silt, sand, and pebbles of chert, igneous, or metamorphic rock fragments. The unit has abundant fractures (generally at oblique angles to the vertical) and occasional slickensides that are coated with iron and manganese oxyhydroxides. Occasional barite precipitates also are present along fractures. The upper part of the glacial drift is more clay-rich and generally contains minor quantities of sand or pebbles and has been locally identified as the Ferrelview Formation of Pleistocene age on the adjacent U.S. Department of Energy property (MK-Ferguson Company and Jacobs Engineering Group, 1990). The residuum (0 to about 38 ft thick) is a highly heterogeneous unit consisting of gravelly clay to clayey gravel with abundant sand and gravel-size chert fragments. In several boreholes, the residuum consisted of weathered chert beds that were interbedded with a plastic, gravelly clay.

Consolidated rocks immediately beneath the overburden consist of the Keokuk and Burlington Limestones of Lower Mississippian age. Detailed borehole data from the adjacent U.S. Department of Energy site indicate that the upper part of these limestones is highly weathered, which results in an uneven bedrock surface (MK-Ferguson Company and Jacobs Engineering Group, 1991). The weathered limestone and overlying residuum can be highly permeable, which has caused the complete loss of drilling fluid while drilling boreholes in this area.

Depths to ground water range from about 10 to 43 ft below the land surface. Generally, the water table is a few feet below the contact between the residuum and the underlying weathered bedrock; however, in some areas near surface drainages the water table is within the residuum. Ground-water flow reflects the surface drainages, and ground water beneath most production lines flows to the north towards Dardenne Creek. A ground-water divide between the Mississippi and Missouri Rivers trends nearly east-west across the south central part of the WSTA (fig. 1).

METHODOLOGY

Based on the frequency and magnitude of the TNT concentrations detected in surficial soil and core samples by the U.S. Army (International Technology Corporation, 1989a), two locations along former TNT production lines 4 (location 1) and 11 (location 2) were selected for collection of soil and water samples from the unsaturated zone (fig. 3). Both of these locations were adjacent to or beneath former red water catch tank houses that were part of the wash house complex. Both sites contained several localized areas (less than about 20 ft across) of red-stained soils that were mostly barren of vegetation, which is indicative of large (a few percent by weight) TNT concentrations.

Four pressure-vacuum suction lysimeters were installed at various depths in the unsaturated zone at each location (table 1). Three lysimeters at each location (LY04, LY05, and LY08 at location 1 and LY09, LY10, and LY11 at location 2) were installed in shallow (less than 6.5 ft) nested boreholes less than a few feet apart. The fourth lysimeter at each location was installed at a deeper depth in an adjacent contaminated area (fig. 3). All lysimeters were placed in inclined boreholes immediately adjacent to red-stained surficial materials. The boreholes were inclined to place the lysimeter cup directly beneath visibly contaminated surficial soils without drilling through them. This placement decreased the potential for highly contaminated surficial materials cascading down the borehole.

Core samples were collected during lysimeter installation and submitted to either the U.S. Army Corps of Engineers laboratory in Omaha, Nebraska, for nitroaromatic compound analysis or to a U.S. Geological Survey laboratory for chemical and mineralogic analyses. Samples for nitroaromatic compound analysis were chilled to 4 °C (degrees Celsius) and shipped overnight to the laboratory. These samples were analyzed for nitroaromatic compounds using the U.S. Environmental Protection Agency (1990) method 8330. Analytes included TNT, 4-Am, 2-Am, TNB, 1,3-dinitrobenzene (DNB), 2,4-DNT, 2,6-DNT, cyclo-1,3,5-trimethylene 2,4,6-trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), and tetryl (nitramine). Detection limits generally ranged from 0.25 mg/kg for TNT, TNB, DNB, and 2,4-DNT to 2.20 mg/kg for HMX. All blank, matrix, and matrix spike recoveries were within the acceptable limits for these analyses.

Table 1.--Description of lysimeter installations

Lysimeter (fig. 3)	Date installed	Drill angle (degrees)	Total depth, angle (feet)	Total depth, vertical (feet)	Base of lysimeter (feet)	Top of silica flour (feet)	Geologic unit
			Locati	on 1			
LY02	08-28-91	12	15.0	14.7	14.2	12.5	glacial drift
LY04	09-11-91	10	6.6	6.5	6.0	4.5	Ferrelview Formation
LY05	09-11-91	18	2.3	2.2	1.9	1.0	Ferrelview Formation
LY08	12-05-91	20	3.5	3.3	2.4	2.1	Ferrelview Formation
			Locati	on 2			
LY06	09-12-91	18	4.0	3.8	3.6	3.6	glacial drift
LY09	12-17-91	17	2.5	2.4	2.3	1.6	glacial drift
LY10	12-17-91	11	3.4	3.3	3.1	2.6	glacial drift
LY11	01-29-92	10	3.2	3.2	3.0	2.1	glacial drift

Water samples were collected from the lysimeters by attaching a hand-held vacuum pump to one of the access tubes to create a vacuum. The access tube was crimped shut and the vacuum left for several days. Water moved from the surrounding soil into the porous ceramic cup if the suction inside the cup was greater than the soil suction.

Preliminary analysis of lysimeter samples was done using the U.S. Army Toxic and Hazardous Materials Agency (1983) method for explosives detection using HPLC (high performance liquid chromatography). However, mass spectral information on some samples indicated potentially large quantities of two known TNT degradation products, 4-Am and 2-Am, which interfered with quantitation of TNT. A method was developed that separates TNT and the amino degradation products through use of a gradient elution profile. Compounds separated by the method are TNT, 4-Am, 2-Am, TNB, DNB, 2,4-DNT, 2,6-DNT, and nitrobenzene (NB). The 2,4-DNT and 2,6-DNT coeluted using this method and if these compounds were detected, the samples were rerun using the U.S. Army Toxic and Hazardous Materials Agency method.

A Hewlett Packard¹ HPLC equipped with a photodiode array was used for the determination of the nitroaromatic compound concentrations. The mobile phase consisted of a gradient elution with a mixture of acetonitrile, water, and methanol that begins with a mixture ratio of 18:80:02 and changes to a ratio of 48:50:02 over 25 minutes. The flow rate was 1.0 mL/min (milliliter per minute). The maximum injection volume that could be used without loss of peak resolution was 150 μL (microliters). The analytical column was an Ultrasphere ODS 5 μm (micrometers), 4.6 mm (millimeters) x 25 cm (centimeters) manufactured by Beckman Instruments. Detection and subsequent confirmation of components were performed by a photodiode array detector and quantitation was based on the chromatogram generated by the detector signal at 250 nm (nanometers). Instrument calibration was achieved with external standards. Chromatograms of analytical standards and a typical lysimeter water sample are shown in figure 4. Sample extracts were prepared by conditioning of an Analytichem 3 cc (cubic centimeters) C-18 solid phase extraction (SPE) cartridge with successive rinses with 10 mL (milliliters) volumes of methanol and reagent-grade water. Approximately 100 mL of the sample water was vacuum eluted through the prepared cartridge. The nitroaromatic compounds were desorbed with 1.0 mL methanol, and brought to 2 mL volume with water. Direct injection of samples onto the HPLC column was used where sample concentrations permitted. Analyte recoveries ranged from 58 percent for TNB to 105 percent for DNB. A conservative estimate of the detection limit based on positively identifiable analytes was 3 μg/L.

¹ Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.



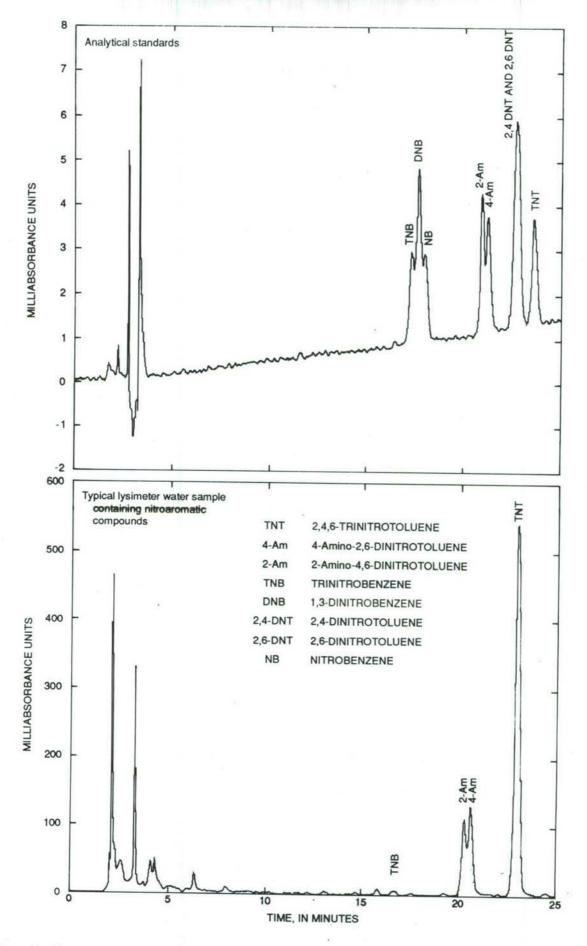


Figure 4.--Chromatograms showing resolution of analytical standards and analysis of a typical lysimeter water sample from this study.



RESULTS AND DISCUSSION

TNT was detected in 18 of the 23 core samples from both locations and in all of the surficial soil samples from locations 1 and 2 (table 2). The surficial soil samples from location 1 contained the largest concentrations of TNT (16,500 to 31,000 mg/kg) detected. These samples were collected from visibly contaminated material overlying lysimeters LY04, LY05, and LY08 (fig. 3). No other nitroaromatic compounds were detected in the surface samples at location 1; however, detection limits for the other nitroaromatic compounds were relatively high because of the large TNT concentrations (table 2). Concentrations of TNT in surface soil core samples from boreholes at this location (LY04, LY05, and LY08) were much smaller (between 583 and 3,070 mg/kg) because the inclined drilling method placed the entry points for these boreholes several feet away from the visibly contaminated area where the surficial soil samples were collected. No data are available for nitroaromatic compound concentrations in core samples from borehole LY02. Surface TNT concentrations were smaller at location 2 where screening indicated concentrations ranging from about 120 to 7,500 mg/kg. Concentrations of TNT in surface core samples from boreholes LY06, LY09, and LY10 were 12.8, 148, and 559 mg/kg (table 2).

Concentrations of TNT decreased substantially within the first 1 ft of depth in all boreholes and concentrations at depths of only a few feet were less than 2 percent of the surface concentrations (table 2). For example, concentrations of TNT in core samples from borehole LY05 decreased from 922 mg/kg at 0 to 0.4 ft to less than 1 mg/kg at 2.0 to 2.2 ft. The actual decrease is much more dramatic because surficial soil samples collected above the cup of lysimeter LY05 had a TNT concentration of 16,500 mg/kg (table 2). Similar decreases were observed in previous investigations at the site (International Technology Corporation, 1989b) and interpreted to indicate that TNT is attenuated within the shallow soil zone and has not migrated deeply within the overburden. An exception is the slight increase in TNT concentrations with increasing depth in borehole LY04. This slight increase is because the borehole at this depth had extended beneath the nearby visibly contaminated surficial materials (fig. 3).

In addition to substantial decreases in TNT concentrations with depth, the concentration of total organic carbon (TOC) tended to decrease with increasing depth in core samples from locations 1 and 2 (table 3). The TOC concentrations in four samples from less than 2 ft deep averaged 0.17 percent by weight compared to concentrations less than the detection limit of 0.05 percent by weight in most samples collected below a depth of 2 ft. Generally the sorption of slightly soluble nonionic organic compounds by soil is related to partitioning into the soil organic matter (Chiou, 1990). Tucker and others (1985) reported that cation exchange capacity and soil organic carbon concentration were factors most critical in determining the degree of TNT sorption by soil. Pennington and Patrick (1990), however, indicated that sorption of TNT was most correlative with extractable iron, cation exchange capacity, and clay content. However, most of these factors are interrelated because the clay-size fraction of soil may contain abundant organic carbon, and cation exchange capacity is a function of both the inorganic and organic content of the soil. In addition, Barber and others (1992) determined that iron concentration was closely related to the organic carbon concentration. Because TNT is a solid at room temperature, much of the large TNT concentrations in the surficial soil samples probably is caused by the presence of finely disseminated particulate TNT in addition to TNT sorbed to organic matter and inorganic minerals.

Small concentrations of TNB (estimated at 0.21 to 46.2 mg/kg) were detected in eight soil samples from boreholes LY04, LY05, LY08, LY09, and LY10. Concentrations were less than the detection limit of 0.25 mg/kg in all subsurface core samples except those from borehole LY09 where the TNB concentrations ranged from 8.03 mg/kg at a depth of 0.9 to 1.1 ft to about 0.21 mg/kg at a depth of 2.2 to 2.4 ft. The detection of TNB in soil core samples was expected because TNB has been shown to be produced by photolysis of TNT in natural water (Burlinson, 1980). The U.S Army also detected TNB in 25 of 53 subsurface soil samples from TNT production areas (International Technology Corporation, 1989b) and in 12 of 16 subsurface soil samples collected at sites where surface TNT concentrations exceeded 1,000 mg/kg.

Five of the core samples (all from location 2) contained small (0.34 to 9.11 mg/kg) concentrations of 2-Am and one surface core sample from borehole LY06 contained a small (0.30 mg/kg) concentration of 4-Am. Except for a small concentration (2.15 mg/kg) of 2,4-DNT detected in the surface core sample from borehole LY08, concentrations of 2,4-DNT or 2,6-DNT were not detected in any of the core samples. The small quantities of RDX and tetryl in the surface core sample from borehole LY08 and RDX detected in the surface core samples from boreholes LY04 and LY05 are

Table 2.--Nitroaromatic compound concentrations in surficial soil and overburden core samples from lysimeter boreholes

[TNT, 2,4,6-trinitrotoluene; 4-Am, 4-amino-2,6-dinitrotoluene; 2-Am, 2-amino-4,6-dinitrotoluene; TNB, trinitrobenzene; DNB, 1,3-dinitrobenzene; 2,4-DNT, 2,4-dinitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; RDX, cyclo-1,3,5-trimethylene 2,4,6-trinitramine; HMX, cyclotetra-methylene tetranitramine; Tetryl, nitramine; all concentrations are in milligrams per kilograms; <, less than; --, no data]

16,500	Sample number (fig. 3)	Sample interval (feet)	Ĭ	4-Am	7. Am	QVE.	a a	E 6				
Surface 16,500 2.6 2.6 2.5 2.5 2.5 2.6 4.00 2.20 Surface 24,900 2.6 2.6 2.5 2.5 2.5 2.6 4.00 2.20 Surface 31,000 2.6 2.6 2.5 2.5 2.6 4.00 2.20 0.0-0.5 583 < 2.6 < 2.6 2.5 2.5 2.6 < 4.00 < 2.20 2.7-3.0 2.22 < 2.6 < 2.5 < 2.5 < 2.6 < 4.00 < 2.20 2.7-3.0 2.22 < 2.6 < 2.5 < 2.5 < 2.6 < 1.10 < 2.20 4-4.49 1.73 < 2.6 < 2.5 < 2.5 < 2.5 < 1.00 < 2.20 5.1-5.3 3.45 < 2.6 < 2.2 < 2.5 < 2.5 < 2.6 < 1.00 < 2.20 5.1-5.3 3.6 < 2.6 < 2.5 < 2.5 < 2.5 < 2.6 < 1.00 < 2.00 < 2.00 < 2.00 < 2.0					IIIV-7	IND	DIND	7,4-DNI	7,6-DNI	KDX	HMX	Tetryl
Surface 16,500 2.6 2.6 2.5 2.5 2.5 2.6 4.00 2.00 Surface 24,900 2.6 2.6 2.5 2.5 2.5 2.6 4.00 2.20 Surface 31,000 2.6 2.6 2.6 2.6 2.6 2.6 4.0 2.20 10.0-0.5 3.73 2.6 2.6 2.6 2.6 2.6 2.6 2.6 2.0 1.10 2.20 2.7-3.0 2.73 2.2 2.5 2.2 2.6 4.10 2.20 2.7-3.0 2.7 2.2						Locat	ion 1					
Surface 24,900 2.6 2.6 2.5		Surface	16,500	<2.6	2.6	205	20	5	,	000		
Surface 31,000 2.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.0 4.20 4.20 4.5 4.5 4.5 4.0 4.20 4.20 4.5 4.5 4.0 4.5 4.5 4.5 4.5 4.0 4.20 4.20 4.5 4.5 4.5 4.0 4.20 4.20 4.20 4.5 4.5 4.0 4.20 4.		Surface	24 900	36	2		3	7	0.7	<10.0	0.77>	<6.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Surface	31,000	0.9	0.22	53	25	2.5	47.6	<10.0	<22.0	<6.5
00-05 583 <26 <26 137 <25 <25 <26 1.10 <2.20 27-3.0 2.22 <26		Saliace	000,15	9.7>	<2.6	2.5	2.5	<2.5	9.7>	<10.0	<22.0	<6.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-	0.0-0.5	583	<26	422	1 37	30.1	30		,		
4.44.9 1.73 < 26 < 25 < 25 < 26 < 100 < 2.20 5.1-5.3 3.45 < 26		2.7-3.0	222	70.1	077	1.37	575	57.5	<26	1.10	<2.20	<.65
5.1-5.3 3.45 <2.26		44.40	1 73	97.5	97.5	<25	<.25	<.25	<.26	<1.00	<2.20	<.65
3.43 <2.26 <2.25 <2.25 <2.26 <1.00 <2.20 4.95 <2.26		51.53	2.45	97">	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
0.0-0.4 922 <26 <26 <27 <25 <26 <27 <220 1.1-1.4 922 <26		63.65	3.43	97.5	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
922 <26 <26 <26 <27 <25 <25 <26 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <20 <td></td> <td>0.000</td> <td>4.93</td> <td>97"></td> <td><.26</td> <td><25</td> <td><.25</td> <td><.25</td> <td><.26</td> <td><1.00</td> <td><2.20</td> <td><.65</td>		0.000	4.93	97">	<.26	<25	<.25	<.25	<.26	<1.00	<2.20	<.65
1.1-1.4 2.49 <26 <26 <25 <25 <25 <26 <1.00 <2.20 2.0-2.2 .70 <26 <26 <25 <25 <25 <26 <1.00 <2.20 0.0-0.2 3,070 <26 <26 <46.2 <25 <25 <26 <1.00 <2.20 2.9-3.1 56.8 <26 <26 <25 <25 <25 <26 <1.00 <2.20 2.9-3.1 56.8 <26 <26 <25 <25 <25 <26 <1.00 <2.20		0.0-0.4	922	<.26	<.26	2 24	>61	36.7			į	14
3,070		1.1-1.4	2 49	361	70.	-		67.5	97">	1.46	<2.20	<.65
3,070 <26 <26 <25 <25 <25 <26 <1.00 <2.20 3,678 <26 <26 <25 <25 <25 <25 <26 <1.00 <2.20 3.56.8 <26 <25 <25 <25 <26 <1.00 <2.20		20.22	6	075	97.5	57.5	<.25	<.25	<.26	<1.00	<2.20	<.65
3,070 <26 <26 46.2 <25 2.15 <26 49.01 <2.20 56.8 <26 <25 <25 <25 <26 <1.00 <2.20		7.7-0.7	0/-	97.>	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
Jo. 6 < 26 < 25 < 25 < 26 < 1.00 < 2.20		0.0-0.2	3,070	<26	<.26	46.2	<25	2.15	<.26	19.01	<2.20	1.32
		1:5	20.0	97">	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65

Table 2.--Nitroaromatic compound concentrations in surficial soil and overburden core samples from lysimeter boreholes--Continued

number (fig. 3)	Sample interval (feet)	TNT	4.Am	2.Am	AN E	DNR	74-DNT	2 6-DNT	RDX	HMX	Terryl
12.9.	(1)			-							,
					Location 2	ion 2					
4	Surface	b120	3	3	;	1	;	ı	1	ı	;
S-5	Surface	005,74	1	15	F.	Ė	1	1	1	1	1
FX06	0.0-0.3	12.8	0.30	0.34	<0.25	<0.25	<0.25	<0.26	<1.00	<2.20	<0.65
	0.5-0.7	11.	<.26	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
	0.9-1.1	.55	<.26	.40	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
	1.9-2.1	<.25	<.26	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
	2.8-3.0	<.25	<.26	<.26	<25	<.25	<.25	<.26	<1.00	<2.20	<:65
TX09	0.0-0.2	148	<.26	9.11	.61	<.25	<.25	<.26	<1.00	<2.20	<.65
	0.2-0.4	11.7	<.26	2.85	19.	<.25	<.25	<.26	<1.00	<2.20	<.65
	0.9-1.1	.46	<26	<.26	8.03	<.25	<.25	<.26	<1.00	<2.20	<.65
	2.2-2.4	97.	<.26	<.26	6.21	<.25	<.25	<.26	<1.00	<2.20	<.65
LY10	0.0-0.5	559	<.26	9.9	2.1	<.25	<.25	<:26	<1.00	<2.20	<.65
	0.8-1.0	<.25	<.26	<.26	<.25	<.25	<.25	<:26	<1.00	<2.20	<.65
	1.8-2.1	<.25	<.26	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65
	3.0-3.3	<.25	<.26	<.26	<.25	<.25	<.25	<.26	<1.00	<2.20	<.65

* Unconfirmed because of matrix interference.

^b Concentration estimated using field screening method.

^e Estimated concentration less than the detection limit.

Table 3.--Carbon concentration of overburden soil core samples from lysimeter boreholes

[all values in percent by weight; <, less than; -, no data]

Lysimeter				
borehole	Sample		Carbon concentration	on
number	interval	Total	Total organic	Total carbonate
(fig. 3)	(feet)	carbon	carbon	carbon
		Location 1		
LY02	1.0-1.6	0.64	0.20	0.44
	1.8-2.2	<.05	<.05	<.01
	3.4-3.7	<.05	<.05	<.01
	4.6-4.9	<.05	<.05	<.01
	5.4-5.7	.05	.04	.01
	7.8-8.4	<.05	<.05	<.01
	8.4-8.8	<.05	<.05	<.01
	10.0-10.3	<.05	<.05	<.01
	11.6-11.9	<.05	<.05	<.01
	13.6-13.9	<.05	<.05	<.01
	13.9-14.1	.40	.16	.24
LY04	1.0-1.5	<.05	<.05	<.01
	4.4-4.9	<.05	<.05	<.01
	5.9-6.3	<.05	<.05	.04
		Location 2		
LY06	0.9-1.1	.39	.39	<.01
	2.9-3.1	<.05	<.05	<.01
	3.1-3.4	<.05	<.05	<.01
LY09	0.4-0.7	.08	.08	<.01
	1.1-1.3			••
	2.1-2.4	<.05	<.05	<.01

probably related to recent U.S. Army training activities at the WSTA. Numerous spent shell casings were scattered on the land surface and RDX and tetryl were not known to be produced at the WSOW (International Technology Corporation, 1989a).

Based on the molar equivalents of the nitroaromatic compound concentrations detected, TNT accounted for more than 90 percent of nitroaromatic compounds detected in the soil core samples, except for subsurface samples from borehole LY09 and one sample from borehole LY06 (0.9 to 1.1 ft). In soil core samples from borehole LY09, TNT accounted for 93 percent of the total nitroaromatic compounds detected in the 0.0 to 0.2 ft sample, but only 5 to 77 percent of the total nitroaromatic compounds detected in samples collected at depths greater than 0.9 ft. Concentrations of 2-Am and TNB accounted for as much as 95 percent of the total nitroaromatic compounds detected in soil core samples from borehole LY09. Concentrations of 2-Am accounted for nearly 50 percent of the nitroaromatic compounds detected in the subsurface soil core sample from borehole LY06 at 0.9 to 1.1 ft deep. Overall concentrations of 4-Am and 2-Am accounted for an average of less than 5 percent of the nitroaromatic compounds detected in the soil core samples.

Semiquantitative analysis of small particulate TNT crystals from location 2 indicated the crystals were nearly pure TNT containing less than 1 percent impurities. Subsamples were collected from the exterior and interior of the crystals to determine the effects of weathering. No large differences were detected between the interior and exterior of the crystals. The crystals were mostly pure TNT but included small quantities of TNB (0.11 to 0.27 percent by weight). None of the particulate samples contained detectable quantities of 4-Am, 2-Am, DNB, 2,4-DNT, or 2,6-DNT.

The two deepest lysimeters at location 1 (LY02 and LY04) have remained dry since installation. The remaining two lysimeters at this location (LY05 and LY08) and three lysimeters at location 2 (LY09, LY10, and LY11) have collected sufficient volumes of water for analysis. Lysimeter LY06 at location 2 only recently (May 1992) began collecting sufficient volumes of water for analysis; however, analytical results were not available at the time of this writing.

Large concentrations of TNT, 4-Am, and 2-Am were detected in water samples from lysimeters LY05, LY08, and LY11 (table 4). The largest concentrations generally were detected in water samples from lysimeter LY08. Concentrations of TNT ranged from 4.1 μ g/L in the water sample from lysimeter LY10 to 6,250 μ g/L in a sample from lysimeter LY08, and concentrations of 4-Am ranged from less than the detection limit in the sample from lysimeter LY10 to 1,740 μ g/L in a sample from lysimeter LY08. Concentrations of 2-Am usually were less than one-half of the 4-Am concentrations and ranged from 5.9 μ g/L in the sample from LY10 to 246 μ g/L in a sample from LY05.

Concentrations of nitroaromatic compounds in the water samples generally were comparable to those detected in the subsurface soil samples, indicating that: (1) substantial sorption of TNT and its degradation products to the soil probably does not occur and (2) aqueous transport of TNT, 4-Am, and 2-Am within the shallow unsaturated zone and through fractures in the underlying glacial drift is likely. For example, mean concentrations of TNT, 4-Am, 2-Am, and TNB in 13 water samples from lysimeter LY05 were 970, 575, 186, and 20.2 µg/L (sample interval of 1.0 to 2.2 ft). The concentrations of TNT in subsurface soil core samples from this borehole (1.1 to 2.2 ft) ranged from 0.70 to 2.49 mg/kg and concentrations of 4-Am and 2-Am were less than the detection limit of 0.26 mg/kg (fig. 5). A similar relation between the concentration of nitroaromatic compounds in soil and water samples was detected in samples from lysimeter LY08 (fig. 5).

Based on molar equivalents of nitroaromatic compounds detected, the lysimeter water samples generally contained a larger abundance of degradation products than the soil core samples. Concentrations of 4-Am and 2-Am accounted for between 6 and 62 percent (mean of 38 percent) of the nitroaromatic compounds detected in water samples. The detection of large quantities of 4-Am and 2-Am in the lysimeter water samples and the near absence of these compounds in the soil and weathered TNT particulate samples indicate these compounds probably are being produced within the upper soil zone and are not readily sorbed to the soil. The lysimeter water samples contained dissolved oxygen concentrations greater than 1.0 mg/L, indicating that the production of the 4-Am and 2-Am compounds probably is occurring by aerobic processes.

Concentrations of TNB in water samples were variable and ranged from less than the detection limit $(3.0 \,\mu\text{g/L})$ in several water samples to $1,130 \,\mu\text{g/L}$ in a water sample from lysimeter LY09 (table 4). Water samples from this lysimeter generally contained the largest concentrations of TNB, which averaged $368 \,\mu\text{g/L}$ in four samples. In these samples TNB accounted for between 38 and 93 percent of the total nitroaromatic compounds detected, indicating substantial photolysis of TNT has occurred. Because photolysis can only occur at the surface, the large concentrations of TNB in water samples from lysimeter LY09 indicate photolysis can be an important mechanism in degrading TNT in contaminated surficial soils at the site, and TNB is not readily sorbed to the soil matrix and migration of large quantities of TNB within the shallow unsaturated zone is possible. No detectable quantities of DNB, 2,4-DNT, 2,6-DNT, or NB were identified in any of the water samples. The lack of DNT isomers (2,4-DNT and 2,6-DNT) in the lysimeter water and soil core samples indicates that DNT has already degraded or was never present in large quantities in the wash house areas.

Concentrations of TNT in the lysimeter water samples exhibit seasonal effects with concentrations tending to peak in December or early January. For example, the mean TNT concentration in samples from lysimeter LY05 increased more than 40 percent from 972 µg/L in six samples collected before December 1991 to 1,387 µg/L in three samples collected in December 1991 and early January 1992 (table 4). Concentrations then decreased to a mean of only 674 µg/L in three samples collected in mid-January and February. The increase in concentrations in December to mid-January may have been related to the initial flushing of weakly sorbed TNT from soils by increased quantities of downward migrating soil water. Pennington and Patrick (1990) suggested that TNT sorption to soil may be controlled in part by dipole interactions with mineral surfaces. Chiou (1990) indicated that sorption of nonionic organic compounds to inorganic minerals is strongly affected by polar interactions with the mineral surfaces. Chiou also indicated that changes in soil humidity affect sorption of nonionic organic compounds. An increase in the available soil moisture would tend to expel TNT sorbed to inorganic mineral surfaces because the TNT could not compete with water for charged surface sites because of its relatively small dipole moment (1.37 for TNT as compared to 1.84 for water). Precipitation and temperature data indicate the

Table 4.--Concentrations of nitroaromatic compound in water samples from lysimeters

[TNT, 2,4,6-trinitrotoluene; 4-Am, 4-amino-2,6-dinitrotoluene; 2-Am, 2-amino-4,6-dinitrotoluene; TNB, trinitrobenzene; DNB, 1,3-dinitrobenzene; 2,4-DNT, 2,4-dinitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; NB, nitrobenzene; all concentrations are in micrograms per liter; --, no data]

Lysimete number										
(fig. 3)		Time	TNT	4-Am	2-Am	TNB	DNB	2,4-DNT	2,6-DNT	NB
					Loc	eation 1				
	10-04-91	1210	1,230	397	215	°106	<3.0	<3.0	<3.0	<3.0
	10-10-91	1140	813	422	246	61.9	<3.0	<3.0	<3.0	<3.0
	10-18-91	1110	1,010	660	242	17.3	<3.0	<3.0	<3.0	<3.0
	10-22-91	1200	816	566	240	12.9	<3.0	<3.0	<3.0	<3.0
	10-31-91	1145	923	603	212	3.2	<3.0	<3.0	<3.0	<3.0
	11-13-91	940	1,040	574	142	<3.0	<3.0	<3.0	<3.0	<3.0
	12-06-91	910	1,340	826	134	<3.0	<3.0	<3.0	<3.0	<3.0
	12-16-91	1230	1,580	816	148	6.9	<3.0	<3.0	<3.0	<3.0
	01-08-92	1148	1,240	661	140	20.5	<3.0	<3.0	<3.0	<3.0
	01-15-92	1005	610	445	129	10.0	<3.0	<3.0	<3.0	<3.0
	01-15-92	1010	598	474	138	^b 5.5	<3.0	<3.0	<3.0	<3.0
	02-06-92	1150	715	540	231	b9.9	<3.0	<3.0	<3.0	<3.0
	02-20-92	1240	697	487	197	⁶ 8.5	<3.0	<3.0	<3.0	<3.0
Mean			970	575	186	20.2			-	
LY08	12-16-91	1235	°3,270	c1,740	°237	b,c<3.0	<3.0	<3.0	<3.0	<3.0
	12-26-92	1115	6,250	616	161	18.0	<3.0	<3.0	<3.0	<3.0
	01-08-92	1200	3,870	821	194	9.8	<3.0	<3.0	<3.0	<3.0
1	01-15-92	1030	3,120	728	157	b<3.0	<3.0	<3.0	<3.0	<3.0
	02-06-92	1145	1,760	631	143	17.1	<3.0	<3.0	<3.0	<3.0
	02-20-92	1251	1,690	593	136	<3.0	<3.0	<3.0	<3.0	<3.0
Mean			3,327	854	171	7.5		(
					Loc	ation 2				
LY09	12-26-92	1100	96.3	23.7	^b 21.0	°85.9	<3.0	<3.0	<3.0	<3.0
	01-08-92	1125	50.1	36.1	b39.7	¢150	<3.0	<3.0	<3.0	3.0
(01-15-92	1100	25.9	36.3	32.2	c106	<3.0	⊲3.0	<3.0	3.0
(02-20-92	1325	9.1	41.9	29.8	°1,130	<3.0	<3.0	<3.0	3.0
Mean			45.4	34.5	31.0	368				••
Y10 (02-20-92	1330	4.1	<3.0	5.9	<3.0	<3.0	<3.0	<3.0	<3.0
Y11 (02-06-92	1115	462	165	40.7	13.5	<3.0	<3.0	-2.0	20
	02-20-92	1320	364	165	35.5	<3.0	<3.0	<3.0	<3.0 <3.0	<3.0 <3.0
Mean			413	165	38.1	6.8				

^a Duplicate sample preserved with mercuric chloride.

^a Not spectrally confirmed.

^c Direct injection.

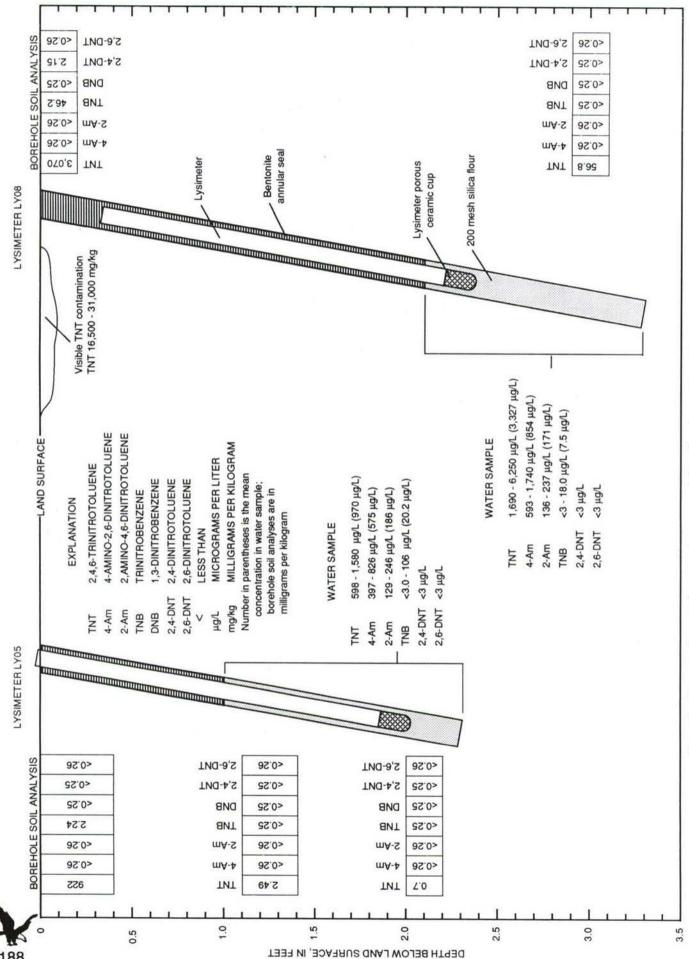


Figure 5.- Concentrations of nitroaromatic compounds in soil and water from lysimeters LY05 and LY08.

increase in soil moisture is not so much related to precipitation as to a substantial decrease in evapotranspiration. Precipitation decreased after late October with monthly mean values of only 2.68, 2.12, 0.53 in. in November, December, and January (fig. 6). However, heavy frosts occurred in late October and early November, causing most of the vegetation at the site to become dormant. The lysimeter sample volume increased in mid-November and reached a maximum in mid-December, when daily mean temperatures were low.

The smaller TNT concentrations in water samples from mid-January and February may represent infiltration of TNT leached from the surface diluted by the increased sustained quantity of soil moisture, before removal of the weakly sorbed TNT from the soil, or both. Concentrations of 4-Am also followed a trend similar to that for TNT in water samples from LY05; however, the variation in concentrations was more subdued. The variation in lysimeter water sample volume and nitroaromatic compound concentrations with season indicates the movement of nitroaromatic compounds through the upper unsaturated zone may occur in a matter of a few weeks; however, additional data (such as deeper lysimeters clustered with monitoring wells and tracer studies) are required to confirm this hypothesis.

SUMMARY AND CONCLUSIONS

Studies are being conducted by the U.S. Army and the U.S. Geological Survey at the Weldon Spring Training Area to determine the potential for migration of nitroaromatic compounds from contaminated surficial soil to the shallow bedrock aquifer. The site is part of the former Weldon Spring Ordance Works that produced TNT and small quantities of DNT during the early to mid-1940's. Much of the site is underlain by a generally unsaturated overburden (0 to 61 feet thick) consisting of topsoil or fill, loess, fractured glacial drift, and residuum. Localized contamination of soils by TNT is present around foundations of many former process buildings. Analyses of more than 5,700 soil screening samples by the U.S. Army indicated sharp decreases in concentrations of TNT with depth. Concentrations of TNT in surface soil samples ranged from less than 1 to more than 81,000 mg/kg but decreased to less than 10 mg/kg at depths of 3 to 4 ft below the land surface. Similar decreases in soil TNT concentrations with depth were detected in surface and subsurface core samples from two lysimeter nests at the WSTA. Surface soil TNT concentrations ranged from 120 to 31,000 mg/kg and concentrations generally decreased to less than 2 percent of the surface values at depths below 2 ft.

Although the concentrations of TNT in soil decreased sharply within a few feet of the land surface, water samples from several lysimeters indicated large concentrations of TNT (4.1 to 6,250 μ g/L) and two known TNT degradation products, 4-Am (less than 3.0 to 1,740 μ g/L) and 2-Am (5.9 to 246 μ g/L). Large concentrations of TNB ranging from less than 3 to 1,130 μ g/L also were detected in the lysimeter water samples.

Data collected in this study, although incomplete, indicate decomposition of TNT within the upper (unsaturated) soil to 4-Am and 2-Am; however, considerable quantities of TNT remain in the upper few inches of soil after more than 45 years of exposure to the environment. Concentrations of 4-Am and 2-Am generally accounted for less than 5 percent of the total nitroaromatic compounds detected in the soil core samples but accounted for between 6 and 62 percent (mean of 38 percent) of the total nitroaromatic compounds detected in the water samples. Locally, photolysis of TNT to TNB at the surface and subsequent transport of TNB within the upper unsaturated zone can be important. The large concentrations of TNT, 4-Am, 2-Am, and TNB in water samples as compared to subsurface soils samples from the unsaturated zone indicate that these compounds probably are only weakly sorbed to these low-organic carbon soils and that the measurement of TNT and its degradation products in the soil, by itself, is not adequate to describe the migration of these compounds in the unsaturated zone. The apparent weak sorption of TNT, 4-Am, 2-Am, and TNB to the soil and presence of fractures within the glacial drift indicates that these compounds are likely to migrate through the unsaturated zone to the shallow bedrock aquifer at the site.

Seasonal effects on the aqueous concentrations of TNT and 4-Am in the unsaturated zone were detected. These seasonal effects probably are related to the initial flushing of the compounds by increased infiltration in the early winter and subsequent dilution of their concentrations by sustained quantities of increased infiltration during the winter. The variation in concentrations also may be attributed to increased available soil moisture caused by decreased evapotranspiration. The effects seem to have little "lag-effect," indicating migration within the upper unsaturated zone at this site may be rapid (on the order of a few weeks); however, additional data are needed to confirm this hypothesis.

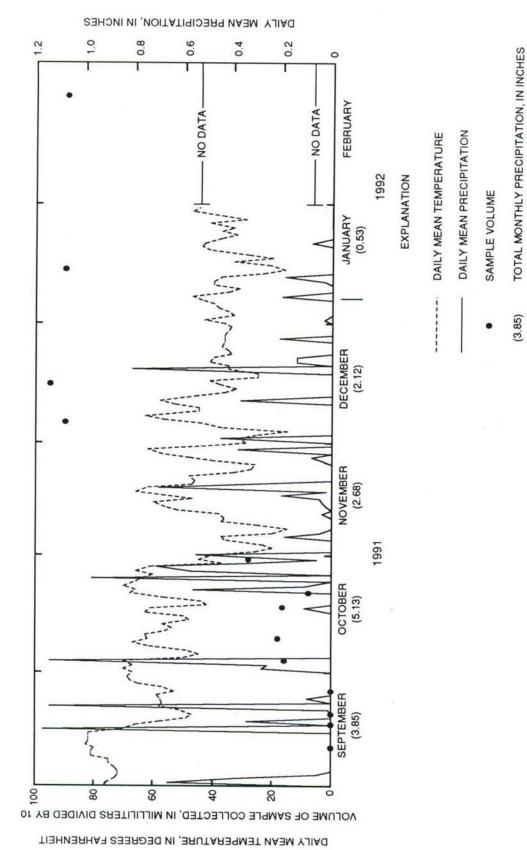


Figure 6.--Volume of sample collected by lysimeter LY05, daily mean temperature, and daily mean precipitation from September 1, 1991, to February 29, 1992 (temperature and precipitation data from D.P. Clum, Jacobs Engineering Group, written commun., 1992).

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THERMAL DESORPTION OF ORGANIC-CONTAMINATED SOIL

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THERMAL DESORPTION OF ORGANIC-CONTAMINATED SOIL

RAYMOND G. GIESE*

INTRODUCTION

With the advent of an increasing number of site cleanup projects, the site remediation industry appears to be taking shape. After many years of intensive site investigations and feasibility studies, the widespread use of on-site remedial technologies is becoming a reality. One possible reason for the long delay of remedial actions involving on-site technology was the lack of experience with and confidence in such technologies. The early embracing of only a few available "tried and true" methods led to costly cleanup estimates and did little to appease the public's concern of health and safety issues. Such issues suggested that the industry needed alternative technologies that were more cost-effective and more readily acceptable to the public. Once such technology is thermal desorption, a process which thermally separates organic contaminants from soil vs. combustion or destruction of the organic contaminants in the soil via the incineration process.

Many hazardous waste sites contain light to moderate levels (less than ten percent) of organic contamination and may not require the "sledgehammer" approach of incineration. Rather, sufficient heat energy can be applied to the contaminated soil to separate or "desorb" the organic compounds from the soil in order to attain treatment standards comparable to incineration. Armed with data of the boiling points and vapor pressures of various organic compounds (those found at hazardous waste sites), and using conventional equipment used in the food processing and road construction industries, early technology developers demonstrated the efficacy of thermal desorption. Today, thermal desorption serves as a cost-effective and publicly-acceptable complement to incineration for the thermal treatment of organic-contaminated soil containing light to moderate levels of contamination.

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THE CONCEPT OF THERMAL DESORPTION

Figure 1 depicts the general theory of thermal treatment systems, including thermal desorption. Thermal desorption is an extension of thermal drying, which is used in a variety of industries such as food processing and oil refineries, to separate water from a base product (such as food or oil). To separate organic contamination, thermal desorption operates at temperatures above the boiling point of water (212°F) but at temperatures less than incineration (generally less than 1000°F) so as not to combust or destroy the organics in the soil.

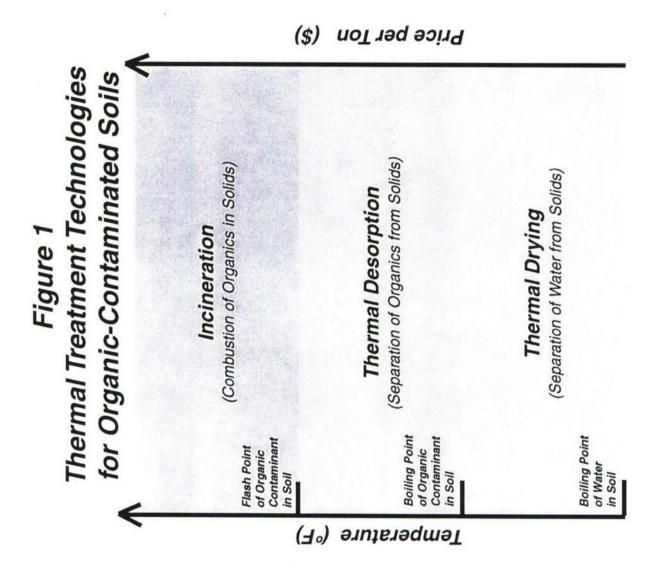
Until recently, the United States Environmental Protection Agency (USEPA) had not officially defined thermal desorption, possibly waiting for the technology to more fully develop. On January 9, 1992 the USEPA published a proposed rule regarding contaminated debris as it relates to the Land Disposal Restrictions. Deep within the proposed rule was USEPA's first official definition of thermal desorption⁽¹⁾:

"Heating in an enclosed chamber under either oxidizing or non-oxidizing atmospheres at sufficient operating temperatures and residence time such that hazardous organic compounds are vaporized and removed from the heating chamber in a gaseous exhaust stream".

Also included in the proposed rule was a definition of thermal destruction(1):

"Treatment in an incinerator operated in accordance with the technical requirements of 40 CFR Part 264 Subpart O or 40 CFR Part 265 Subpart O, boilers or industrial furnaces operating under either interim status or a RCRA permit, or in other thermal treatment devices, such as pyrolysis units operating under interim status in accordance with the requirements of 40 CFR Part 265 Subpart P".

It appears that USEPA is promoting a more flexible application of thermal desorption so as to hasten the cost-effective cleanup of projects that involve light to moderate levels of organic contamination in soil. The distinctions between thermal desorption and thermal



destruction are obvious. Whereas, thermal desorption is a broadly defined, flexible, physical description, thermal destruction is a rigidly defined, regulatory-driven description. With the increasing number of remediation projects using thermal desorption, it appears that USEPA will maintain its flexible view of the technology and encourage its use to hasten cleanups.

TYPES OF THERMAL DESORPTION SYSTEMS

Several technology developers have devised methods to thermally desorb organic contaminants from soil. Generally, the technologies can be classified three ways:

- Type A Systems consist of convective heat transfer utilizing heated air to make intimate contact with soil and desorb the organic contaminants. Rotary dryers are the most common Type A system and are designed to effectively and safely treat organic concentrations of up to three percent.
- Type B Systems rely on conductive heat transfer using a sealed rotary cylinder with the feed material tumbling inside and the heat source on the outside. The contaminated soils, coming in contact with the inner wall of the cylinder, are conductively heated and allow for desorption of organic contaminants of up to ten percent in most cases. The rotary calciner is an example of a Type B system, although holo-flight screw systems can also be classified as such.
- Type C Systems utilize a radiant heat source other than direct flame, such as microwave or infrared, and typically use a conveyor belt to move the contaminated soils through the system. However, it is yet to be determined if these systems are technically capable and cost-effective on a large scale.

Further discussion of the types of systems will focus on the rotary dryer and rotary calciner since both systems have been proven to be <u>both</u> technically capable and economically viable complements to incineration within the thermal treatment market.

Figure 2 and Table 1 compare the characteristics of rotary dryer and rotary calciner thermal desorption systems, as well as rotary kiln incineration to allow for a comparison (because of its widespread use at underground storage tank sites, the "Soil Roaster", as it is commonly known, is listed separately on Table 1. However, the basic components are essentially the same as the rotary dryer technology). The important distinctions are the operating temperatures, level of soil mixing, and amount of air flow (or use of an inert carrier gas). These system parameters thus define what portion or niche of the organic "spectrum" (refer to Figure 3) each system approaches a best-fit application (in terms of technical capability, cost-effectiveness, and public acceptance).

Soil Roaster Systems

Environmental industry publications are full of ads for transportable thermal remediation systems that can treat organic-contaminated soil (refer to Figure 4). The compact one-trailer units are capable of processing 2-10 tons per hour of lightly-contaminated soil containing petroleum products such as gasoline, diesel fuel, jet fuel, heating oil, and other volatile aromatic compounds.

Contaminated soil is screened to remove debris and large particles while the remaining soil is fed into the unit. The soil is tumbled in a small rotary dryer (approximately 10 ft. in length by 3 ft. in diameter) at temperatures ranging from 450°F - 650°F for three to seven minutes. Organic hydrocarbons in the soil are volatilized and are carried to the secondary treatment unit which oxidizes the organic airstream at 1400-1600°F for approximately 0.5-1.0 seconds. Final particulate removal occurs via a cyclone or baghouse prior to the release of the airstream to the atmosphere. The treated soil exits the dryer and is cooled with water to control dust before being backfilled on-site. Total petroleum hydrocarbon levels in the soil are generally reduced to less than 10 parts per million (ppm).

The shorter retention time and lower operating temperatures of these smaller "soil roaster" systems limit the application of these units to smaller underground storage tank sites. Any significant contamination (usually greater than one percent organics) or larger site sizes requires the use of a larger rotary dryer system. The "soil roaster" systems are not

Conceptual View of Thermal Treatment Systems Figure 2

Characteristics

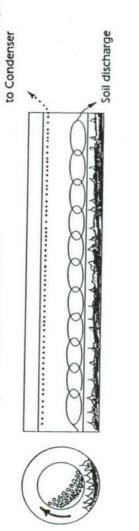
Hydrocarbon Vapors

Rotary Dryer Desorption

Flights

to Treatment

- Low Temperatures
- High Air Flow Significant Soil Mixing
 - No Refractory Separation
- Inert Gas Flow
- Minimal Soil Mixing
 - No Refractory Separation
- Medium Temperatures



Vapors to Secondary

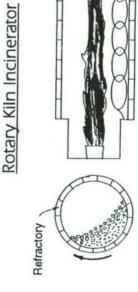
Oxidizer

Soil Discharge

Hydrocarbon Vapors

Rotary Calciner Desorption

Soil Discharge



- High Temperatures Moderate Air Flow
 - Minimal Soil Mixing Refractory
 - Destruction



Table 1
Comparison of Features
On-Site Thermal Treatment Systems

System Feature	Small "Soil Roaster"	Rotary Dryer	Rotary Calciner	Incineration
Primary Heat Transfer Method	Convection	Convection	Conduction	Radiant
Soil Throughout (tons/hr)	2-10	25-50	5-15	25-50
Maximum Soil Feed (inches)	5".	.2	5".	.2
Soil Residence Time (minutes)	3-7	7-30	30-70	20-40
Operating Temperature (°F)	400-650	400-900	006-009	1800-2200
Contaminant Vapors Treatment	Secondary Oxidizer	Secondary Oxidizer	Condensed	Secondary Oxidizer
"Best Fit" Applications:				
Type of Contaminants	Petroleum	Petroleum/RCRA	RCRA/TSCA	RCRA/TSCA
Level of Contamination	Light	Light-Moderate	Moderate	Moderate-Heavy
Size of Site (tons)	<5,000	>5,000	>10,000	>15,000

Figure 3
Spectrum of Organic Contaminated Soil
On-Site Remediation Projects

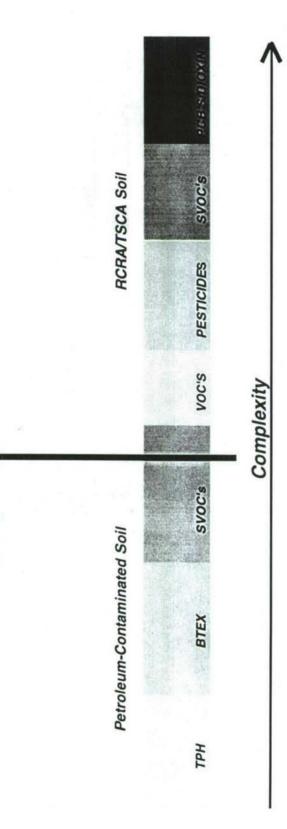
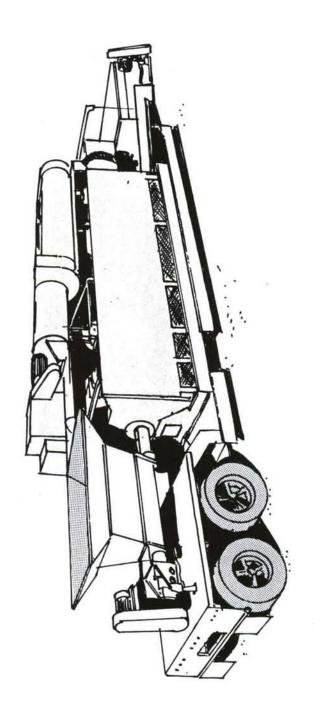


Figure 4 Soil Roaster



Source: Progressive Development Intl. Inc. Hartland, WI



designed to treat soils containing RCRA or TSCA wastes and should not be applied in such cases.

Rotary Dryer Systems

Larger rotary dryer systems (refer to Figure 5) are capable of processing more moderately contaminated soil (generally up to three percent organics) for most petroleum-related organics and a wide range of RCRA-type contaminants such as volatile organics (halogenated and non-halogenated), pesticides, and many semi-volatile organics compounds (halogenated and non-halogenated). Screened contaminated soil is fed into the rotary dryer via feed hoppers and a belt conveyor. The dryer is typically 35 feet in length by 6.5 feet in diameter, allowing for a retention time of up to thirty minutes. It is desirable to have significant mixing and tumbling of the soil in the drum in order to allow for intimate contact with the heated air and to increase the soil temperature to a range of 650-900°F. The treated soil is cooled and dedusted by a water spray before being backfilled on-site (or stabilized in a pugmill prior to backfill if heavy metals are a concern).

In most systems, the organic airstream exits the dryer and moves through a cyclone to remove particulates, through a secondary treatment unit to oxidize the organics (1400-1600°F at 0.75-1.0 seconds), and subsequent movement through a baghouse for final particulate removal. If the soil contains chlorinated compounds a wet scrubber is added to remove acid gases prior to the release of the airstream to the atmosphere. Target organic compounds are generally reduced to levels below 1 ppm, and in many cases are non-detectable subsequent to treatment, depending upon soil type and initial contaminant concentrations⁽²⁾.

Rotary dryer systems have demonstrated to be cost-effective, complements to incineration for many organic-contaminated sites. These systems are capable of processing up to 50 tons per hour and are best applied to sites in excess of 5,000 tons.

Rotary Calciner Systems

Figure 6 depicts the rotary calciner system which is an excellent complement to incineration for sites containing organics of up to ten percent concentration. Since most

Figure 5 Rotary Dryer Desorption

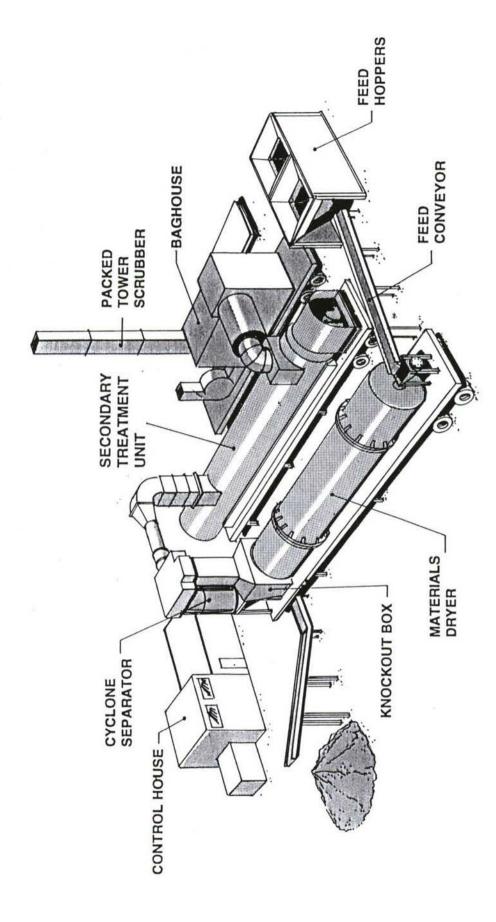
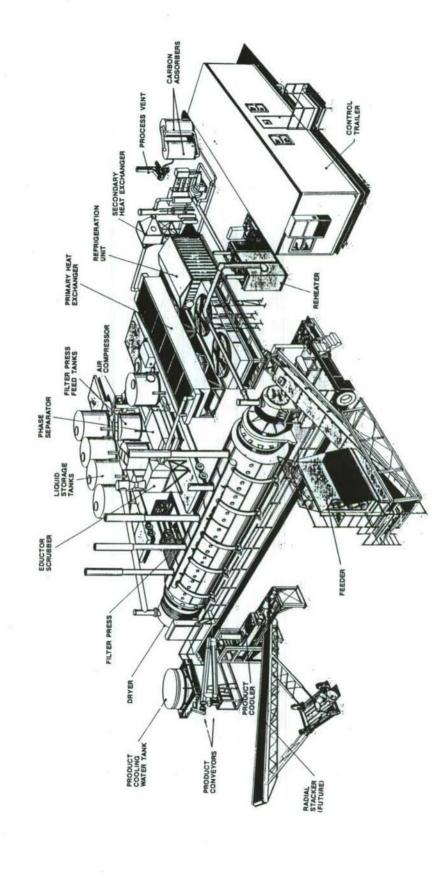






Figure 6 Rotary Calciner Thermal Desorption (X*TRAX[™] System)



Source: Chemical Waste Management, Inc. Oak Brook, IL



calciners operate in an oxygen free environment it can successfully handle a wide range of RCRA/TSCA wastes, including PCBs.

Feed material (either solid or pumpable sludge) is fed into the dryer, which is a sealed rotating cylinder. The feed material tumbles inside the cylinder while the heat source is on the outside, preventing combustion products from coming in contact with the wastes. The heated solids are discharged from the dryer and backfilled on-site after dedusting (the system allows for stabilization if required).

An example of a rotary calciner system that is used to treat hazardous waste is the X*TRAXTM thermal desorption system developed by Chemical Waste Management, Inc.. Organic vapors are carried via a nitrogen gas in the X*TRAX system and passed through a liquid scrubber where entrained solid particles are removed and the gas stream is cooled to its saturation temperature. The scrubber also removes a portion of the volatilized organics. Recirculated scrubber water passes through a phase separator and continuously discharges a bottom sludge containing solids, water, and organics. The sludge is dewatered using a filter press. The dewatered solids are either returned to the feed stream or disposed of off-site.

The scrubbed gas passes through heat exchangers where it is cooled, producing liquid condensate which contains the organics (shipped off-site for incineration or recycled if appropriate). Gravity separated water is used to cool and dedust the treated soil exiting the calciner. The cooled carrier gas passes to a recirculation blower and is heated prior to returning to the calciner. A process vent pulls off 5-10% of the nitrogen gas prior to the blower which passes through a particulate filter and carbon adsorber prior to release to the atmosphere.

Target organic compounds are generally reduced to less than 1 ppm in the treated soil, and, like the rotary dryer, are non-detectable in many cases, depending upon initial soil type and pre-treatment organic concentrations⁽²⁾. Rotary calciner systems have proven effective for moderately contaminated sites, especially for treatment of soils containing PCBs, and are capable off processing 5-15 tons per hour. Rotary calciner systems are

best applied to treatment of RCRA/TSCA soil contamination, and at sites containing more than 10,000 tons of soil.

SELECTION OF THE APPROPRIATE SYSTEM

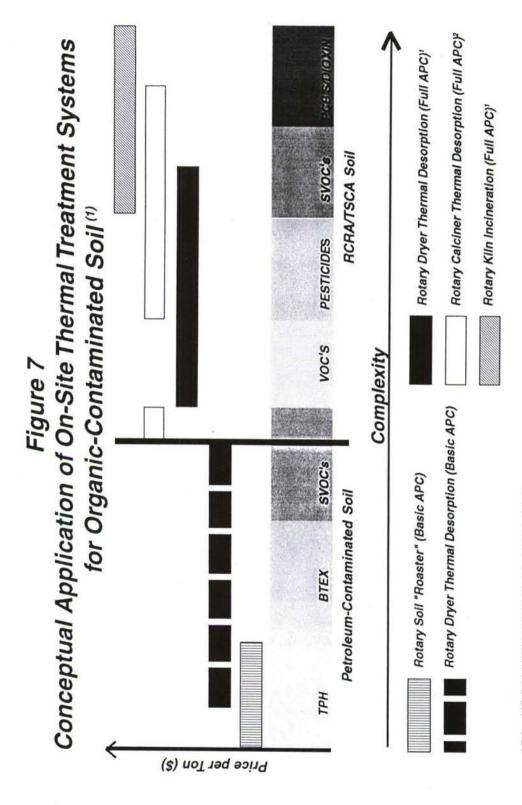
Figure 7 depicts a general application of thermal desorption systems (incineration is included for comparison). Based upon thermal desorption projects completed to date, the graph reflects the likely applications of the respective systems. Please note that the figure reflects the "niche" for each system based upon <u>both</u> technical capabilities and economic viability. However, in order to ensure selection of the most appropriate system project design personnel must pay heed to site specific conditions including:

- Volume of soil requiring treatment
- Moisture content of soil
- Soil matrix
- Type and amount of contaminant(s)
- Treatment standard(s) to be achieved

Only through a detailed analysis of these criteria (in addition to issues regarding timing of the project and public acceptance) can project design personnel determine what system will be most appropriate from <u>both</u> a technical and cost standpoint. Generally, it is best to complete a treatability study to assist in the final determination. Results from the treatability study, coupled with the guidelines outlined in this paper, should result in the selection of the most appropriate thermal desorption system.

COSTING FOR THERMAL DESORPTION

Very seldom do project design personnel compare cost estimates on an "apples to apples" basis. For planning purposes, it is suggested that project costs be divided into three tasks (refer to Figure 8): 1) Items that relate to preparing the site prior to the arrival of the thermal treatment system (Box A); 2) Items that relate to the operation of the thermal treatment system (Box B); and 3) Items that are associated with site closure after operation of the thermal treatment system (Box C). As Figure 8 suggests, total project costs are affected by many issues other than waste processing. In turn, true waste processing-related costs (Box B items) can be significantly affected by site specific



APC - AIR POLLUTION CONTROL EQUIPMENT

Basic: Cyclone, secondary oxidizer, cooling tower, baghouse

Full: Cyclone, secondary oxidizer, cooling tower, baghouse, scrubber

► FulP: X*TRAX: Scrubber, condensing unit, carbon

 Graph reflects <u>both</u> technical capability and economic viability of respective thermal treatment systems. Final selection is dependent upon site specific conditions.



Figure 8

On-Site Thermal Treatment Brainets

	On-Site I nermai Treatment Projects Price Line Items	atment Projects Items	
Box A +	Box B +	Box C =	Total Price
■ Excavation	Mobilization	 Stabilization (if required) 	Total of All 3
 Waste Preparation 	 Permitting / Work Plans 	 Final waste placement as backfill on site 	
Consumables (PPE, carbon, etc.)	 Site Preparation Assume all site prep including foundations done by customer Utilities supplied to the Battery 	 No long term monitor- ing /care included 	
	Limits of project	 Includes verification sampling 	90
	 Waste Processing Labor Depreciation, rental, etc. 	n.	
	 Includes any necessary H₂O treatment and discharge 		



Also includes any contaminant

disposal charges

Demobilization

REFERENCES

(1) Federal Register, 40 CFR Parts 148, 260, 261, et al. Land Disposal Restriction for Newly Listed Waste and Contaminated Debris; Proposed Rule, Thursday, January 9, 1992.

USEPA, Office of Emergency and Remedial Response, Engineering Bulletin, EPA/540/2-9/008, May 1991. Thermal Desorption Treatment.

both a cost and technical standpoint. Project design personnel are advised not 1to exceed the limits of the respective systems, and should rely on valid site-related data and a treatability study to help make final system selection.

conditions as detailed previously. Project design personnel should be ready to supply all project-related information to technology vendors in order to ensure a "true" cost estimate and a valid comparison of technologies.

CASE STUDY: RE-SOLVE, INC. SUPERFUND SITE

The Re-Solve, Inc. Superfund Site is located in North Dartmouth, Massachusetts. The six-acre site is bordered by residential areas, wetlands, and forested areas. Previous activities on the site included chemical reclamation, resulting in contamination of the soil and groundwater with PCBs, acids, and organic and inorganic liquids and solids. Chemical Waste Management (CWM) was contracted to use its patented X*TRAX thermal desorption technology (rotary calciner) to treat the soil and reduce the PCB contamination to below 25 ppm.

Site management was complicated by poor site access, extensive soil contamination, and a high groundwater table, making movement of equipment and excavation of soil difficult at best. Since the entire site is contaminated, excavation and stockpiling of contaminated soil was required in order to accommodate mobilization of the X*TRAX system. As the project proceeds, CWM will rotate the position of site control trailers, etc. in order to allow for excavation of additional contaminated soil.

During May, 1992 CWM conducted a full-scale proof-of-process of the X*TRAX technology. CWM processed 500 tons of soil with PCB concentrations ranging from 200-300 ppm. As a result of treatment via the X*TRAX thermal desorption process, CWM was able to reduce PCB concentrations in the soil to non-detectable levels (detection limit of 1 ppm), with no toxic decomposition of the PCBs into dioxins or furans. CWM expects full-scale production to commence by the fall subsequent to review and approval of a proof-of-process report submitted to USEPA.

CONCLUSION

Thermal desorption is a cost-effective and technically capable complement to incineration for the thermal treatment of a wide variety of organic-contaminated soils. However, site specific conditions will dictate which thermal treatment system is most appropriate from

DEPLETED URANIUM RISK ASSESSMENT AT ABERDEEN PROVING GROUND

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Introduction

Approximately two years ago, the Test and Evaluation Command (TECOM) at Aberdeen Proving Ground (APG), Maryland, began a study to determine the long-term fate of depleted uranium munitions (DU) in the environment. Testing of DU munitions results in deposition of DU on soils and vegetation and in surface water surrounding impact areas at APG. While the munitions testing program is important to the defense of the United States, the Army also considers maintaining the quality of the ecosystems surrounding the munitions test sites important. TECOM is sponsoring this study in order to quantify health risks, if any, to humans and deleterious effects, if any, to plants and animals in the surrounding ecosystem due to DU munitions testing. TECOM's interest is focused by the following inquiries:

- · Does DU migrate from the impact areas?
- Does DU adversely affect terrestrial and/or aquatic ecosystems at APG or in Chesapeake Bay?
- · Does DU pose a threat to recreational and/or commercial resources?
- Is there any significant risk of human health effects due to DU testing?
 Several ecosystem or partial ecosystem models are presented in the following discussion. These models were developed in order to investigate the fate of DU in

the APG environment with respect to the interests of TECOM. The aquatic model was modified from a model of carbon cycling developed by Baird and Ulanowicz (1989). Our aquatic model is more site-specific than the Chesapeake Bay-scale of Baird and Ulanowicz (1989) primarily to address the above questions. A terrestrial model was also developed that focuses on DU ingestion by deer. The deer model was based on models described by the NCRP (NCRP 76, 1984). The present terrestrial model uses white-tailed deer as the ecosystem component of interest and, therefore, describes only the dynamics that affect deer. The model is general enough, however, to be extended to more complex terrestrial ecosystems just as the aquatic model is.

Sensitivity of these models to different input parameters was also considered and will be discussed below. The value of sensitivity analysis is that several simulations of DU concentration in the different ecosystems can be conducted and the parameters that are not important to the outcome (i.e., not sensitive) can be identified. Data about the less important parameters is therefore less important than data about more important parameters, and the sampling scheme to validate the model can be simplified. Sensitivity analysis also gives investigators a general perspective of how error in parameter values affects the outcome of model simulations. The results of sensitivity analyses on both ecosystem models will be discussed below.

Conceptual Models

Importance of Models. Models of complex ecosystems and the processes that occur within ecosystems provides an efficient means of estimating the flow DU through the components of interest. Simulations of how the ecosystem responds to different conditions or how the ecosystem behaves through time can be conducted many times using models, whereas lifetimes would be spent in the field observing

the same systems. Simulations using environmental conditions significantly different than present conditions can also be conducted. Models are useful tools in guiding data collection to answer specific questions. For example, results of simulations might show that certain parts of an ecosystem are adversely affected by low concentrations of contaminants, or that some part of the ecosystem tolerates large ranges of contaminants with little adverse effect. Examining an ecosystem by using models developed specifically for the ecosystem of interest is an effective and relatively simple way to gain important insights into detailed behavior of complex ecosystems.

Models can also be applied inappropriately, suggesting system behavior not truly observed in nature. There is an obvious need to check models of systems against their natural counterparts by direct field observations. The models below were developed after careful consideration of the natural systems involved, but also incorporate estimated values when little or no information about parts of the ecosystem was available. Uncertainty or sources of error in the models was estimated qualitatively as well as determined mathematically in order to show the weaknesses in the models that were developed and to suggest the parts of a model that are most or least affected by a contaminant. The models described below are based on actual processes occurring in the systems, on field observations as often as possible, and were subjected to rigorous uncertainty analysis. Both models appear to give a reasonable image of the aquatic and terrestrial ecosystems at APG.

We developed "box" models for the aquatic and terrestrial ecosystems. Box models are relatively common for modeling purposes and provides one tool with which investigators can simplify a complex system and view the system and the interactions of its components graphically. Interacting components (such as omnivorous fish eating smaller fish) can be easily shown using the box model approach. The boxes in these models monitor the amount (concentration) of a

substance in the box. Box models can show concentration with time, and several boxes can be defined so that flow between the boxes is quantified. The transfer of contents from one box to another (one ecosystem component to another) can be described mathematically as a time derivative of the concentration or as a simple ratio of the material of interest in one component to that in another. If time derivatives are used, then the box model represents the mass transfer or concentration change through time in a given box or set of boxes. At some point the concentration change per unit time reaches a steady state and remains constant with additional time. The concentration ratio or bioconcentration factor (BCF) assumes that steady state exists instantaneously and reflects an "equilibrium" condition. Bioconcentration factors are used when biokinetic information is not available for a particular component or when "batch" tests are the source of data about a component.

Figure 1 shows how the equations for a single box in a model are constructed. The component of interest is "boxed," then the flux of material in and flux out are determined using the transfer functions. At the beginning of a simulation the boxes can be zero or non zero. As time progresses in the simulation, the concentration in the box of interest and the boxes in general change according to the transfer function. The concentration in the box eventually comes to equilibrium or steady state and sometimes decays back to initial conditions. Figure 2 gives the concentration at three different times in one box shown in Figure 1.

Aquatic Model. The model of the aquatic ecosystem at APG was derived from the Chesapeake Bay ecosystem. The aquatic model is based on a deterministic carbon flow model developed by Baird and Ulanowicz (1989). The carbon model (Baird and Ulanowicz, 1989) shows carbon flux through the Chesapeake Bay along most of its reach. Mesohaline ecosystem components are identified and the interactions between components are quantified by species. The model will be

refined throughout the study to incorporate field sampling data. Thus the model is still under development.

We modified the carbon model in several significant ways. First, we limited the model to a smaller scale than Baird and Ulanowicz (1989) so that effects, if any, on the APG ecosystem can be observed. Since the largest effect from DU fragments, if any, will be observed within or near the APG reservation boundary, the model omits components and interactions that would not be expected within the APG boundary.

Second, we changed carbon intake to uranium intake. This modification involved finding new values of the transfer coefficients either from existing data sets or from literature values. The former are rare at present, but some data do exist (e.g., Chassard-Bouchaud, 1983; Ahsnullah and Williams, 1989). Most transfer coefficients were estimated from published results of several researchers and resulted in large ranges in the values for specific parameters. The large ranges in the uncertainty values also mean that results of simulations vary a great deal. During model development, the large uncertainties were used without trying to minimize their contribution; field data will be collected to minimize the uncertainties and to make model simulations more site specific to APG.

The APG aquatic model is best described as a box model and is shown in Figure 3. Each box is an ecosystem compartment that is roughly equivalent to a species or several species of interest. For example, the compartment "Benthic Invertebrates" in Figure 3 corresponds to blue crab. Transfer between compartments is shown by the arrows in Figure 3 and represents the actual flow of U from one box to the next. The transfer rates, as mentioned above, are not well known for all parts of the system that is modeled. Instead, steady state values (BCF's) of the rates are assumed when the actual rates are not known. Assuming the steady-state BCF's also implies that the transfer rates come to steady state

quickly in time, and approximates an actual transfer rate relatively closely. A BCF of 10 in any box indicates that the amount of U in the compartment is 10 times as great as the surrounding water. Values less than unity suggest that no bioaccumulation occurs in the particular compartment, whereas values greater than unity indicate that bioaccumulation does occur by some mechanism.

The initial conditions require a DU concentration in the water. The input concentration is propagated through the system for a set time interval. Simulations in this report were conducted for test periods of several hundred days to about 300 years. The components and transfers were constructed so that a unit input (e.g., mg-U/L) could be followed graphically, and the units in each compartment were either mg-U/L or mg-U/kg-dry matter depending on the type of component. Input water concentrations could then be bounded using the solubility of DU penetrators or measured DU concentrations in water. In addition, "nominal" and "worst case" types of simulations could be conducted relatively easily.

Three possible DU concentrations were used for the simulations of DU migration through the aquatic system. The lowest initial input value was 0.003 mg-U/L and was obtained from environmental sampling data collected at APG. This was the largest concentration measured at APG and came from a groundwater sample near Ford's Farm. The highest input value is about 0.08 mg-U/L and represents equilibrium solubility of schoepite (UO₂(OH)₂·H₂0) with no dilution due to stream or groundwater flow. Equilibrium solubility with no dilution is unrealistically high because of the extremely unlikely occurrence of this type of dissolution. A mid-range value of 0.008 mg/l was also used to show the effects of a relatively high yet plausible concentration of DU.

Bioconcentration factors and transfer rates were estimated from the literature. Transfer of material from one component to another depends on rate or steady-state processes that increase or decrease the amount of DU in the

components. Transfer rates and BCF's are related to the biokinetics of the component and may also depend on species, sex, age, and season. Thus, a set of or transfer rates or BCF's for a component is not necessarily the same as a set for a different component. The extreme variability in some cases was due to different experimental conditions and/or to differences in measuring methods, the kinds of measurements made (e.g., whole body versus specific organs or tissue). We made little attempt to select a "best estimate" for the values, but instead we used the entire published range of values. Using the entire range resulted in large uncertainties in the final results and will be discussed in more detail below.

Estimates of consumption rates and/or amounts were taken from the carbon balance work (Baird and Ulanowicz, 1989). The rates were modified only slightly because of the small amount of data on the consumption of U by different animals in the model and also because consumption of carbon are likely to result in intake of DU if any is available.

Uncertainty and Sensitivity Analyses. Figure 3 shows the schematic of the APG aquatic model. The transfer of DU through the system depends on the bioconcentration factors or transfer rates as discussed above. Estimates for many of these factors or rates were derived from literature values and cover a large range. For example, the concentration factor for U in phytoplankton from water ranges from 16 to 1700 (Mahon, 1982; Trabalka and Garten, 1983). Since the output of the models depends on the input values, the model was used with different input values in each iteration. The results of multiple runs of the aquatic model gave nominal values for the bioconcentration factors (BCF) and are shown graphically in Figure 4. The effects of the nominal BCF values on the aquatic consumers in the model (i.e., Omnivorous and Carnivorous Fish, Crabs, Shellfish, and Zooplantkton compartments) are shown in Figure 5. Figure 5 also suggests that there is slight accumulation in fish, crabs, and shellfish but significantly more accumulation in

zooplankton. Other results show that the labile sediment is a major sink of DU in this system, and that the sediment comes to steady state at a slow rate compared to other compartments. Figure 6 shows the accumulation rate of four compartments and that the steady state value is reached almost immediately in the model runs. In the same simulations, however, DU accumulation in labile sediment takes about 100 years to reach steady state (Figure 7).

The results of the simulations suggest that DU migrates within the system and affects some compartments more than others. The compartments of importance to understanding DU migration in this ecosystem are the zooplankton and the labile sediment, then the interactions of these compartments with the rest of the system. The simulation results also show that the compartments that preferentially accumulate DU should be considered more carefully in the field sampling. The field sampling plan will focus on those compartments that accumulate DU and will also obtain data from other compartments such as the crabs, fish and shellfish that will test the model's validity. Field data from APG will provide the information needed to refine the aquatic model so that quantitative determinations of DU in the aquatic ecosystem can be made.

Deer Model. A model of ingestion of DU by deer was developed to approximate the terrestrial ecosystem and one likely pathway that could affect human health. A large population of white-tailed deer inhabit the APG reservation, and the deer are hunted yearly to maintain the size of the population. Deer also die of natural causes at APG as anywhere else in nature. The deer model is shown in Figure 8. The model is similar to the aquatic model above but is less complex. Possible DU pathways for deer are through soil ingestion, ingestion of plant material that is coated or contains DU, and through water that deer drink. Each pathway is shown in Figure 8. The deer model is based on radionuclide

uptake by battle (NCRP 76, 1984). The cattle ingestion rates of water and vegetation were modified to reflect lower consumption rates and smaller amounts consumed by deer. Also, soil ingestion is not included in the NCRP model but was added to the APG deer model.

The deer model is similar in construction to the APG aquatic model in that there are several compartments represented, and interactions between the boxes depend on bioconcentration factors and/or transfer rates. DU enters the deer system in two forms, dissolved in the surface water and groundwater and solid from fragments of DU munitions.

Most parameters input into the model were based on literature values. whereas some values (e.g., groundwater flow rate) were measured in other studies at APG. Estimates of the transfer rates and/or bioconcentration factors were required for the deer model as for the aquatic model. Estimates were derived for bioconcentration factors of DU in soil relative to vegetation and in vegetation relative to deer tissue. The estimates varied considerably, sometimes over one to two orders of magnitude. Deposition rates and locations area also variable. DU is deposited in the surface water and on soils of the impact area, but the proportion of DU landing in soil or water is not known. Aerial photos show that up to 40% of the impact area could be surface water. Based on the aerial photos, different deposition proportions were used in the simulations: 60% on soil, 40% in water; 50% on each; 40% on soil, 60 % in water; and all on either soil or in water. Leaching rates control the amount of DU dissolving and moving into groundwater and were estimated using soil properties measured from APG soils. Deer mortality rates (non-hunting) and body masses were estimated from Moen and Severinghaus (1981), Fuller (1990), and Fryxell et al (1991), and harvesting rates were determined from hunting counts in 1991.

The deer model is simple enough to conduct relatively elaborate Monte Carlo simulations using the range of input values to determine how sensitive the model is. Ingestion through water the deer drink was the most important pathway for DU, and soil ingestion was next most important. The contribution of DU from the vegetation the deer eat was small due in part to a small bioconcentration factor in plants relative to soil concentrations. Estimates of DU resuspended on plant however, are not well known and probably contributes to more ingestion of DU than indicated in the simulations. The important parameters are the ones that determine or control the concentration of DU in water, including leaching rates, dissolution of DU, amount of DU deposited in water, and how much water the deer drink. Soil ingestion rates and possible concentrations of DU in soils, particularly in "hot spots" or areas of locally high DU concentration, are needed to refine the contribution of this pathway to the migration of DU in the terrestrial system. Also, a more complete terrestrial model is being developed to test DU migration in realistic simulations. The completed terrestrial model will resemble the complexity of the aquatic model and should provide a more complete picture of DU migration in the terrestrial system at APG.

Conclusions

Models that quantitatively describe the interactions of components of ecosystems provide tools to estimate the migration of DU through the aquatic and terrestrial systems at APG. The results of simulations using these models suggests the important compartments and transfers in establishing potential harmful effects to humans, The simulations also provide information on which compartments are important to sample in the field.

While ecosystem models are valuable tools, the same models have been developed around estimates of critical parameters include most of the transfer rates

and /or BCF's. The estimates come largely from the published literature on U in ecosystems and thus cover a variety of natural and experimental conditions. A large degree of uncertainty about the estimated values us reflected in the large variation in results of the simulations. Data from field sampling in the APG environment will allow a refinement of the models of DU migration and will result in a tool for a quantitative risk assessment of the DU on the range at APG.

The models will be refined and used to evaluate the risk of adverse effects, if any, in humans and the environment due to DU fragments in the impact area at APG. The models also will guide the development of environmental sampling planned for the APG area, and should result in efficient and cost-effective sampling to monitor and document DU movement into the environment. Management decisions will benefit from the use of the models to determine the effects, if any, of DU testing on the environment at APG, personnel working in the impact area, and the general public. For example, management at TECOM earlier recognized the value of ecosystem models in assessing the potential impact of the DU program on the environment at APG. The DU study, including the models, is an important part of an integrated environmental monitoring plan for the Aberdeen and Edgewood areas of APG. Completion of the models, sampling, and risk assessment will provide information to TECOM management about the DU program and will assist TECOM management in ensuring the protection of the terrestrial and aquatic ecosystems within which APG operates.

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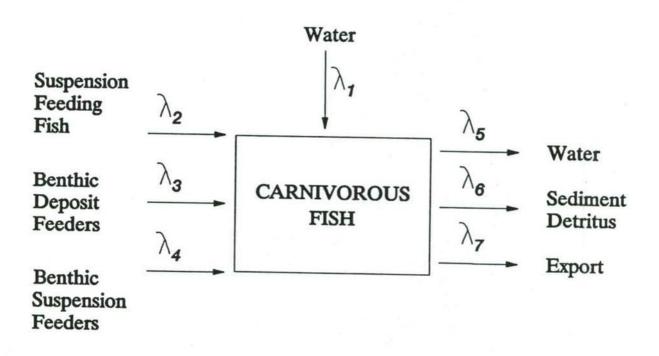


Figure 1. Conceptual model of DU transport through a single compartment, Carnivorous Fish, in the APG aquatic model. Each λ represents a rate of change in DU concentration (mg-U/kg dry mass) due to that pathway.

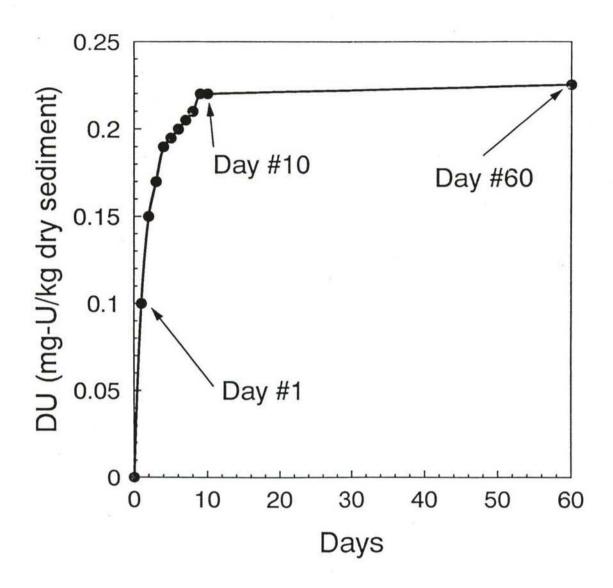


Figure 2. Predicted DU concentration in labile sediment relative to overlying water. Units are arbitrary since relative concentrations are used.



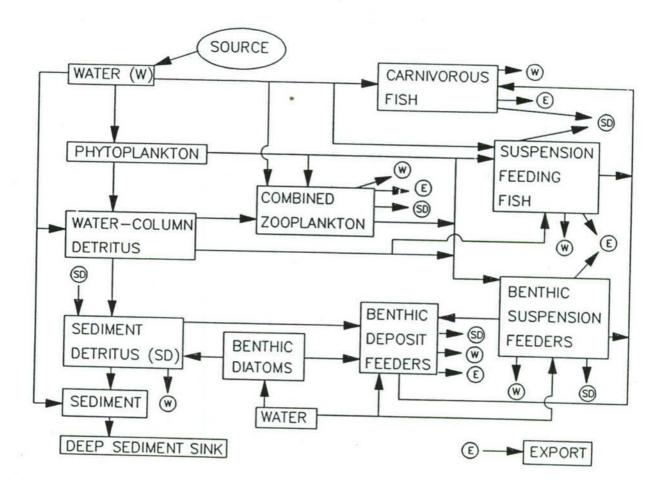


Figure 3. Conceptual model of DU transport through the aquatic system at APG.

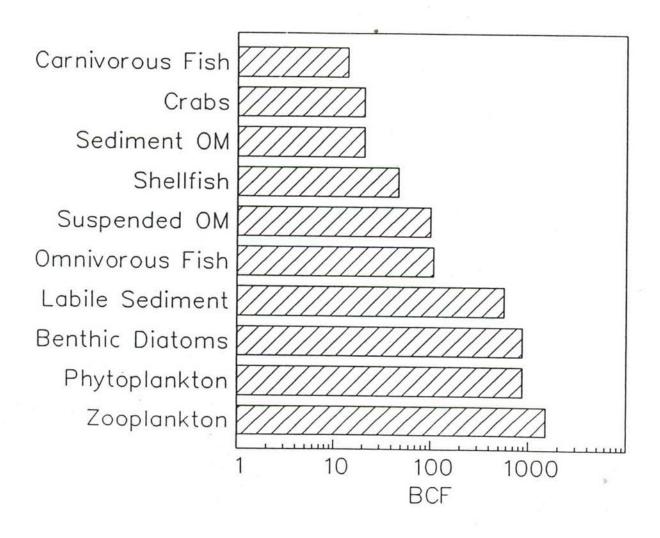


Figure 4. Predicted concentrations of compartments in preliminary APG aquatic model relative to water (i.e, BCF's) after 1000 years.



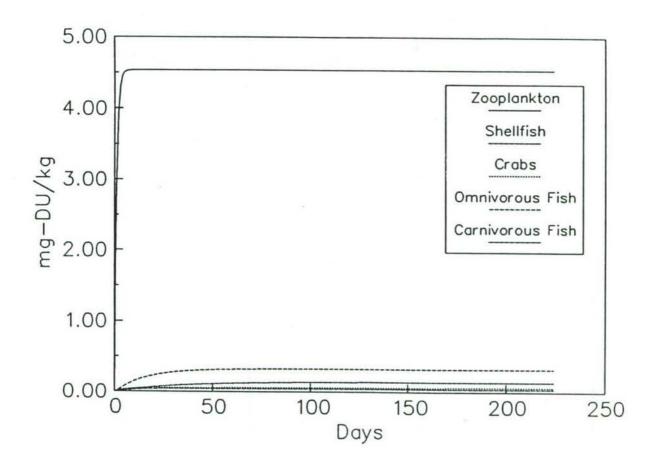


Figure 5. Predicted DU concentrations in aquatic consumers from preliminary model.

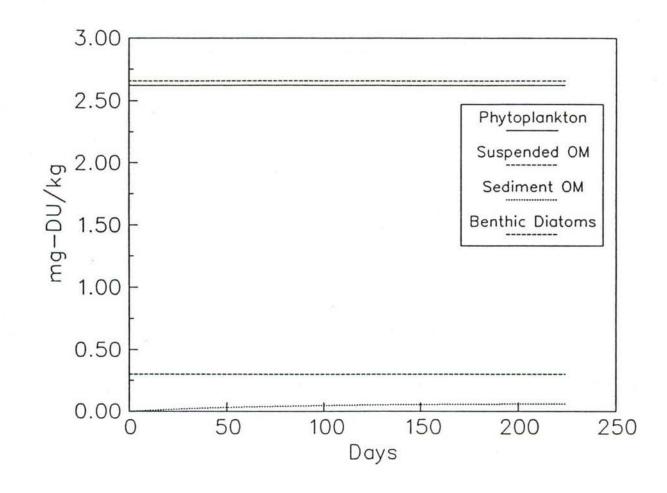


Figure 6. Predicted DU concentrations in primary food sources for aquatic consumers from preliminary model.



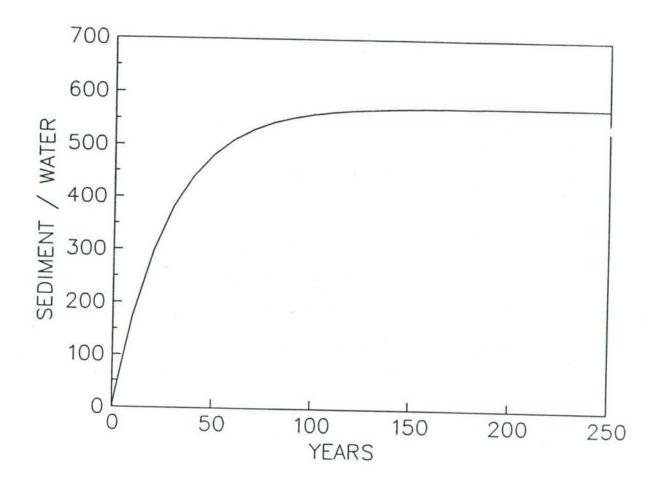


Figure 7. Predicted DU concentration in labile sediment relative to overlying water from preliminary model.

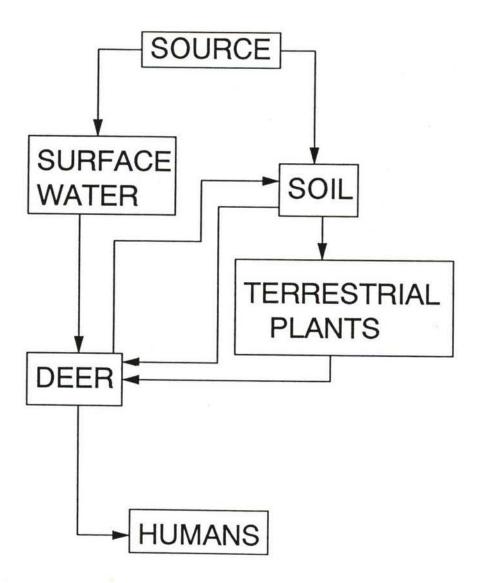


Figure 8. Conceptual model of DU migration through terrestrial environment to deer and to humans.



IN SITU DETECTION OF FUEL CONTAMINATION IN SOIL BY FUEL VAPOR SENSORS

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ABSTRACT

A laboratory scale evaluation study was conducted at the Naval Civil Engineering Laboratory to select the type of in situ fuel vapor sensor that can detect Navy fuels, primarily JP-5 and diesel fuel marine (DFM), in soil. The types of vadose zone sensors evaluated in this study included metal oxide semiconductor (MOS), diffusion, and aspirated MOS. A laboratory scale system was designed to determine the performance of these sensors for detecting Navy fuels. This system consisted of a fuel vapor flux chamber, a PC computer based sensor control and data acquisition setup, and an organic vapor analyzer. This organic vapor analyzer was modified, and a calibration procedure was developed to determine the total hydrocarbon concentrations in fuel vapors during experiments. Known amounts of fuel were added to the vapor flux chamber and data were collected to determine sensor response time, and detection capability. Additional experiments were conducted to determine the effects of variables such as temperature, more volatile fuel (JP-4), and mixed fuels on sensor response. The collected data indicate that the MOS sensor has better fuel vapor detection capabilities for Navy fuels than other sensors. This sensor indicated a rapid response time, was able to detect relatively low concentrations of fuels and was not strongly affected by normal temperature variations. This commercially available sensor is also suitable for integration into sensor networks for monitoring large sites.

INTRODUCTION

The U.S Navy maintains more than 5000 underground storage tanks (USTs) including more than 600 bulk tanks and extensive pipeline facilities. These facilities handle various types of fuels including bulk quantities of Navy unique fuels: diesel fuel marine (DFM) and JP-5. Past fuel leaks from these facilities have caused soil and ground water contamination at several Navy installations 1.

Depending on the site specific conditions, in situ vadose zone sensors that detect the presence of fuel vapors in soil can

be integrated into monitoring networks for remote and continuous monitoring of large sites ². These networks can also be used to provide an early warning of fuel leaks. The potential leak detection applications include bulk underground tanks and high capacity pipelines for which there is a lack of leak detection techniques.

These sensors are primarily in use for detecting gasoline vapors in soil. The purpose of this study was to determine the performance of vadose zone sensors for detecting JP-5 and DFM.

DESCRIPTION OF SENSORS

Three types of vadose zone sensors were selected for this evaluation study.

METAL OXIDE SEMICONDUCTOR SENSOR (MOS)

The MOS sensor consists of a thin film of tin oxide supported on a silicon wafer, an embedded heater, and connection points for power and signal transmission. The hydrocarbon vapors are adsorbed on the tin oxide surface and change the resistance of the sensor indicating presence of fuel vapors. The sensor signal is processed in the control unit that consists of a power supply used with a 110 volt AC supply, and signal conditioning board with adjustments for alarms. Sensor output is 0 to 5 volts analog signal. For actual field application, the sensor is installed inside a vapor monitoring well and is connected to a centrally located control unit. The MOS sensors are used in several applications including alcohol detectors, combustion monitoring, and natural gas detection 3.

ADSISTOR (DIFFUSION) SENSOR

This sensor consists of a resistor that is encapsulated in a thin film of proprietary organic polymer. The hydrocarbons are diffuse into the polymer film and cause a change in the electrical resistance output of the sensor. For field application, the sensor is installed in the monitoring well and is connected to the centrally located control unit.

ASPIRATED MOS

In this configuration of the MOS sensor, MOS sensor is located inside the central control unit rather than in a monitoring well. A small pump in the control unit transfers fuel vapors from monitoring well to the sensor through small diameter plastic lines. The pump operates in conjunction with a valve that automatically switches from on port (monitoring well) to the other in a programmed sequence. The control panel also contains a microprocessor that controls pump operation and performs data processing and calibration.



LABORATORY SCALE SYSTEM FOR SENSOR EVALUATION

A laboratory scale setup was fabricated to obtain sensor response data for the detection of Navy fuels. This setup is shown in Figure 1. A brief description of major components follows:

- (a) Fuel Vapor Flux Chamber. This chamber consisted of a 12 * 12 inch cylindrical container with concentric 2-inch diameter slotted PVC screen. Pea gravel was placed in the outer chamber and sensors were installed inside the PVC screen (sensor chamber). During experiments, fuel was added to the pea gravel in the outer chamber and the sensors were exposed to the fuel vapors that migrated into the sensor chamber through the PVC screen.
- (b) Sensor Control and Data Acquisition System. This system consisted of a COMPAQ personal computer, a 12-bit analog/digital converter timer board , and a multiplexer amplifier board. During experiments, sensors were connected to the this system for automatic data collection and control.
- (c) Organic Vapor Analyzer (OVA). A flame ionization detector based OVA was used to determine total hydrocarbon concentrations (THCs) in fuel vapors to which sensors were exposed during experiments. During experiments, vapor samples (0.15 ml) were periodically withdrawn from the sensor chamber and were injected into the OVA. The unit was modified to allow sample injection and was calibrated with methane in air mixtures. This procedure involved the development of a standard plot of known calibrant concentrations VS. corresponding OVA response as signal peak height. A typical plot is shown in Figure 2 and the figure shows a linear correlation between calibrant concentrations and peak heights. During sensor evaluation tests, the OVA was recalibrated prior to each experiment.

The general procedure to obtain sensor response data for detecting fuel vapors included: (a) computer setup for data collection, (b) sensor baseline data collection prior to fuel addition, (c) OVA calibration, (d) fuel addition to the gravel, (e) sensor response data collection at 5 minute intervals, (f) periodic injection of vapor samples into OVA for determinations of THC, and (g) removal of sensors from flux chamber at the completion of step (e) and response data collection during fuel desorption from sensors.

The sensor data was analyzed to provide information on sensor response time, detection capability and desorption time. The desorption time data is an indication of sensor's ability to response to decreased fuel concentration.

RESULTS AND ANALYSIS

MOS AND ADSISTOR SENSORS - TESTS WITH JP-5



Three tests were conducted with 20-,40-, and 80-ml JP-5 fuel. The MOS sensor response, volts vs time, observed during these tests are shown in Figure 3. During these three tests with the MOS sensor, the first sensor reading taken five minutes after fuel addition, indicated a sensor response to fuel vapors. The response continued an upward trend for about an hour. The Adsistor sensor response data during JP-5 tests are shown in Figure 4. For the 20 and 40 ml tests, the adsistor response did not increase for about 15-20 minutes after fuel addition, followed by a slow increase.

The THCs obtained from the OVA during these tests are shown in Figure 5. The first samples from each test (samples taken 5 minutes after fuel addition) indicated concentration of 23, 43, and 80 ppm as methane for 20, 40 and 80 ml fuel test, respectively. A positive vapor flux into the sensor chamber was observed for about 50 minutes and then the concentrations leveled off at approximately 150, 225, and 285 ppm for the three tests.

The MOS response data during desorption tests are shown in Figure 6. (Sensors were removed from the vapor flux chamber for desorption tests and reductions in sensor output signals were expected.) The figure indicates rapid reductions in sensor signals. During the first 15 minutes, the MOS signal had an average reduction of about 80 percent. The Adsistor data during desorption are shown in Figure 7. The figure shows a downward trend but as compared to the MOS, the trend is considerably slower. After 15 minutes, the Adsistor signals showed an average reduction of about 30 percent as compared to 80 percent for the MOS.

These tests indicated that although both sensors can detect JP-5 fuel vapors, the response time for MOS was shorter than that for Adsistor. The OVA data indicated a rapid flux of fuel vapors into the sensor chamber immediately after fuel addition and the MOS sensor was able to detect this flux better than the Adsistor sensor.

MOS AND ADSISTOR SENSOR - TESTS WITH DFM

Three tests were conducted with DFM using 20-, 40-, and 80-ml fuel and similar to the tests with JP-5, the MOS sensor detected fuel vapors within 5 minutes of fuel addition whereas, the Adsistor showed a slower response. Both sensors showed lower signals as compared to signals with JP-5. The THC data from the OVA also indicated lower vapor concentrations in the chamber. These concentrations were only about 50 percent of those observed with JP-5.

The results of desorption tests indicated a rapid response for MOS sensor and during the initial 15 minutes, the MOS signal dropped by about 85 percent as compared to a 50 percent reduction in the Adsistor signal.



JP-5 TEST WITH ASPIRATED MOS

This test with JP-5 was conducted to compare the performance of MOS and aspirated system. Both sensors showed similar response times for fuel detection and desorption.

JP-4 TEST WITH MOS AND ADSISTOR SENSORS

The sensors response to 5-ml JP-4 is shown in Figure 8 that indicates a rapid increase in sensor signal output from both sensors. A significant improvement in the performance of the Adsistor sensor was observed during this test as compared to previous tests with DFM and JP-5. As in case of the MOS, the Adsistor detected fuel vapors within 5 minutes of fuel addition. The results obtained during desorption were also similar for the two sensors and both sensors showed an almost identical and rapid reduction in output. JP-4 fuel is more volatile as it contains lower boiling point petroleum fraction than JP-5 and DFM. This was also shown by the THC data obtained from OVA during this test. The THC level in the sample taken 5 minutes after fuel addition was 1,298 ppm vs 23 ppm for JP-5.

EFFECTS OF OTHER VARIABLES (MIXED FUEL AND TEMPERATURE) ON MOS AND ADSISTOR SENSORS

A test was conducted to determine the effects of mixed fuel on sensor performance and in this test a fuel mixture containing 20-ml JP-5 and 20-ml DFM was used. The sensor signals observed during this test were lower than those observed during tests with "pure" fuels. However, the sensors basically followed similar trends during fuel detection and desorption as compared to previous tests with JP-5 and DFM.

Another test was conducted to determine the effect of ambient temperature variation on sensor readings. This test was conducted for 12 hours and the temperature varied from 72.4°F to 83.3°F during this period. Sensors were not exposed to any fuel vapors during his time. The MOS signal showed an increase of 0.03V and the Adsistor showed a higher increase of 0.14V. The Adsistor was indicated to be more sensitive to temperature variations than the MOS sensor. The embedded heater in the MOS sensor maintains a more uniform operating temperature.

CONCLUSIONS

The results of the study indicated that the MOS and the Adsistor sensors were able to detect DFM and JP-5 vapors. However, the MOS sensor consistently produced a higher signal response almost immediately it was exposed to JP-5 or DFM fuel vapors, while the Adsistor had a slower response. The MOS sensor also exhibited a shorter desorption time, indicating a better response to changing fuel concentrations. The ambient temperature

variations had a smaller effect on the MOS sensor.

The MOS sensor showed a rapid response time ,less than 5 minutes, to both JP-5 and DFM fuels. The sensor was able to detect relatively low concentration of fuel, less than 20 ppm as methane. The sensor can be integrated into monitoring networks for site monitoring and can be used with automated data collection hardware.

The performance of the Aspirated sensor was comparable to the MOS and both showed a rapid response for detecting fuel vapors. However, since the Aspirated system uses small plastic lines to transfer vapors from monitoring wells to the sensor, it has a limited application at large sites that will require rather long plastic lines.

The fuel type had a strong effect on the performance of sensors and can be related to the extent of fuel volatility. The sensors had a lower response to DFM as compared to JP-5. The highest response was observed for JP-4 which is considerable more volatile. The THC data from the OVA showed a similar trend of fuel volatility.

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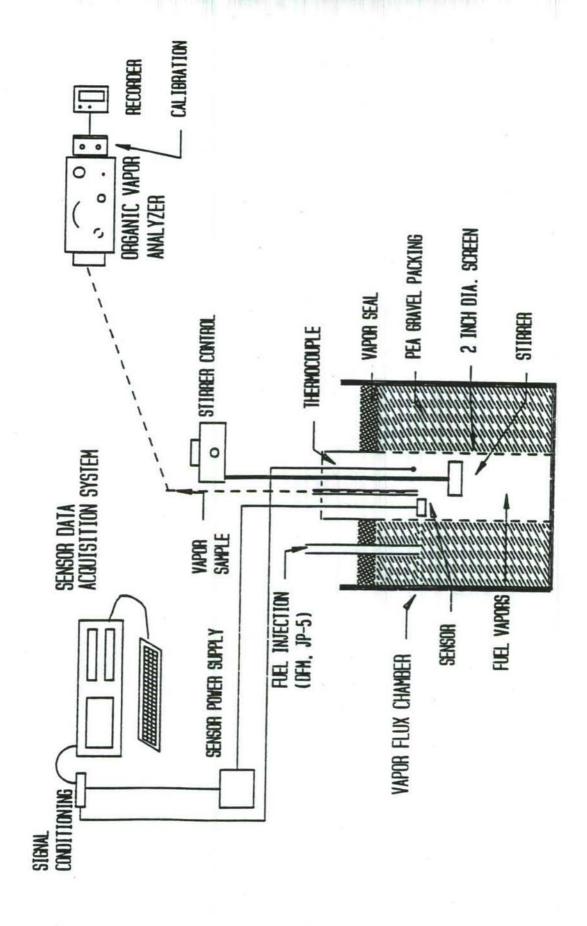


Figure 1. Diagram of laboratory scale setup for sensor evaluation

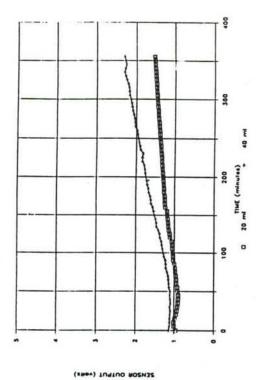


Figure 4. Adsistor sensor response to 20 and 40 ml JP-5 fuel.

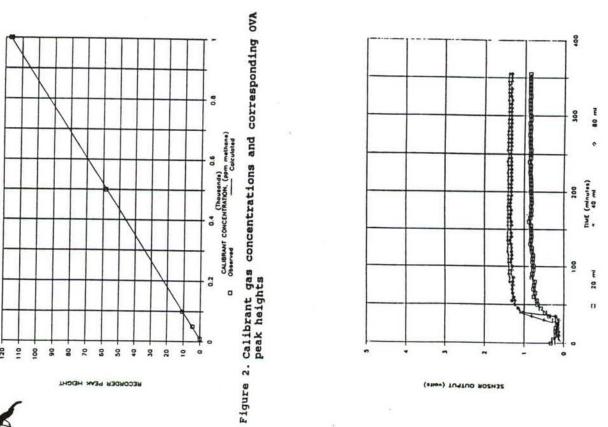
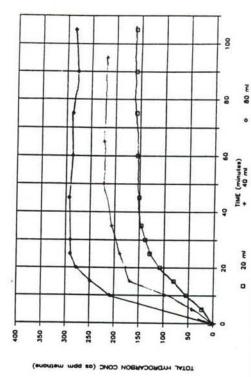


Figure 3. MOS sensor response to 20, 40, and 80 ml JP-5 fuel.



SENSOR OUTPUT (volts)

Figure 5. Total hydrocarbon concentration measured by OVA in tests with 20, 40 and 80 ml JP-5 fuel.



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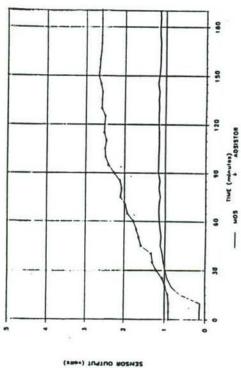


Figure 8. MOS and Adsistor sensor response to 5 ml JP-4 fuel.

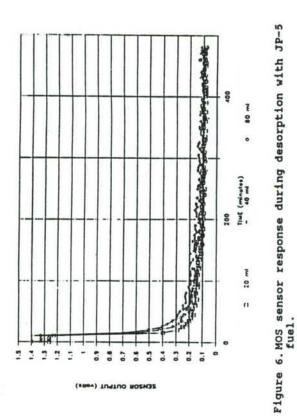


Figure 7. Adsistor sensor response during desorption with JP-5 fuel.



DEVELOPING EXPANDED CAPABILITIES FOR THE SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS)

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ABSTRACT

The current design for the Site Characterization and Analysis Penetrometer System (SCAPS) uses a 18,143 kg (20 ton) truck with a 35-mm (1.4 in) diameter instrumented, hollow, steel rod as the soil penetrator. The rod is designed with a cross-sectional area that will allow the rod to take the full 178 kN loading that the reaction mass can generate. The maximum interior opening in the rod is 18 mm (0.7 in). This type of equipment can penetrate to a depth of approximately 50 m (150 ft) in normally compacted soils. Tip resistance on the rod will generally range from 2.8 to 5.9 MPa (406 - 856 psi) for typical sands and from 95 to 950 kPa (13 - 138 psi) for clays. The typical values for sleeve or sidewall friction range from 1 to 3 percent of the tip resistance for sands and from 3 to 6 percent for clays. Intermediate soil types will produce intermediate penetration resistance values. The limit of penetration occurs when the advancing rod has built up a total resistance equal to the reaction mass on the ground surface. If the rod does not encounter an impenetrable soil zone such as a rock layer or a cemented soil the increase in the total sidewall friction as more rod is put down in the soil becomes the major factor limiting penetration.

A novel technique has been developed to overcome much of the sidewall friction on the rod end to reduce the force required to advance the rod to a specific depth. Air or an inert gas under pressure is forced out through holes in the wall of the rod into the interface between the rod and the soil, decreasing the friction resistance as the rod is pushed into the soil. Initial field tests indicate reaction force reduction of up to 50 percent. This new probe design is important because it means the existing SCAPS truck can be used to reach greater depths in normal soils and that future equipment designed for the 50-m penetration range can be lighter (and less expensive) with rods that can accomodate additional or bulkier instrumentation.

Other enhancements to the SCAPS system include vacuum-hardened tool steel used in the push rods, increasing the push rod diameter to further increase its stress capacity, development of an angled push capability, and additional sensor developments. These enhancements and improvements will be incorporated into the next generation of SCAPS equipment.

INTRODUCTION

Background.-- The static cone penetrometer test (CPT) has been utilized in Europe for over half a century, particularly in Belgium and the Netherlands, where much of the soil is soft clay. The popularity of CPT has spread rapidly to many countries, and is commonly used for foundation design investigations. Its use has become standardized both in Europe and the United States (ASTM, 1991).

The CPT can provide soil stratification profiling based on values obtained from cone tip resistance, sleeve friction, and friction ratio. The CPT thus provides an accurate continuous in-situ index of subsurface soil layering. Quantitive information relative to soil strength and classification is not only accurately obtained, but is highly repeatable. The cone penetrometer instrumented with electronic strain gages is designed and used for such quantitative measurements.

The method used to push the electric cone penetrometer into the ground consists of a hydraulic jacking system. These rigs are most commonly mounted in heavy duty trucks which provide the dead weight needed for the reaction force. The reaction force needed to push the penetrometer increases as the depth of push increases, and often the practical limiting factor for increased depth of push is either the strength of the push rod itself (typically 1.4" or 35.6 mm diameter), or the practical, legal highway weight of the truck. Some rigs utilize screw anchors to develop reaction force over the actual vehicle weight. Soil anchors can produce a reaction force of 200 kN (45,000 lbf). A 200 kN thrust will typically result in penetration depths of 25 to 30 meters (80 to 100 feet) in stiff clays and dense to medium dense sands. Greater depths may be achieved in lower consistency soils, and of course lesser depths (if any) are achieved in cobbles and boulders (de Ruiter, 1981).

Purpose.-- Any method that will increase the push depth without overstressing the steel penetrometer rod or requiring the push rig weight be increased is an improvement for the cone penetrometer system. The purpose of this report is to discuss areas where the next generation of penetrometer equipment can be improved to provide better performance more economically. This report describes some of the enhancements being developed and incorporated into the SCAPS system.

SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM

A full description of the current configuration of the SCAPS truck is given in Cooper and others, 1991. The current truck is well suited for application to a majority of investigations at hazardous waste sites, but there are increased capabilities that are desirable.

In most of the investigations that have been undertaken with the SCAPS unit the target depth of investigation was less than 10 m (30 ft.) The SCAPS truck in its current configuration has been used to push to depths of over 130 feet (45 m) in alternating sands and clays in the coastal plain. There is a definite need at some sites to go to greater depths because of a dense sinking contaminant or a deep water table.

Many hazardous wastes site are former industrial operations with storage tanks and pipelines still in place. Skid-rigged rams have been used with the SCAPS instrument package to get in close to storage tanks and in between buildings. Experience on these sites has shown that there is a definite need for a penetrometer that can be pushed at an angle so that sensors and samplers can be pushed under building foundations and under tanks and pipelines.

Penetrometers are primarily designed for applications in soils, but on waste sites it is usual to have soils with buried obstructions that are not apparent even from geophysical investigations. For example, it is not uncommon to find construction debris on the same site with wastes that have contaminated the soil. A typical SCAPS operation can relocate holes in the area of the debris so that all needed data can be obtained although some persistence may be required to find holes in the debris that allow the deeper soil layers to be investigated. However, pushing through debris is not desirable due to the increased wear and tear on the penetrometer rod. There is a definite need for hardened tools that can be used without being damaged in areas where the rods are going to be scraped and gouged by buried obstacles.



Figure 1. The SCAPS truck in the field.

AIR INJECTION PROBE

One enhancement of the SCAPS system is an air-assisted (air injection) push rod technique. Air or an inert gas under pressure is forced out through holes in the wall of the rod into the interface between the rod and the soil. This method allows a reduction of force required to advance the rod by overcoming much of the sidewall friction on the rod. Most of the gas moves upward along the rod surface and reduces the friction similar to an air bearing. When groundwater is present, the wet soil is fluidized to create a mud lubricant layer on the rod. By injecting the air above the instrumented section of the rod (above the lower 2m (6 ft) none of the sensor measurements will be affected. Initial field tests have been conducted with results indicating a 30 to 50 percent reduction in force required to advance the push rod can be achieved.

The initial prototype air injection tool consisted of a modified "dummy" probe, which is a 30 cm section of solid steel cylindrical push-pipe with an integral 60 degree cone tip. The cylinder was internally bored out to provide a continuous chamber from the threaded end to the tip. Four 1.5 mm (1/16 in.) circumferentially-spaced holes were placed approximately 4 cm (2.2 in) above the tip, and an internal threaded plug through which a 6.3 mm (1/4 in.) aluminum tube protrudes comprise the original air injection design. The tool was threaded onto the push pipe, the tube was connected to a tank of compressed air, and initial field penetrations were made to determine the applicability of using air injection to reduce the vertical component of force necessary to push a rod into the soil. The yoke on the penetrometer rams was instrumented with strain gages to allow the force required to drive the rod to be continuously measured. Data was taken by noting the depth of the rod tip from an automated string potentiometer and the corresponding force on the rams.

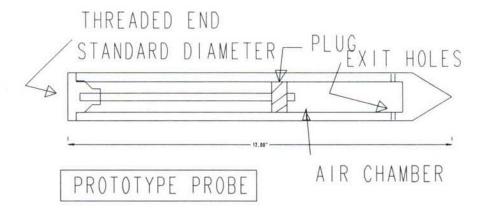


Figure 2. Prototype Air Injection Tool



Field testing consisted of side-by-side soil penetrations using the same air injection probe. No compressed air was used for the first penetration, and compressed air was used for the second penetration. Depth versus hydraulic ram force measurements were made, and compressed air (nitrogen gas) pressures were varied for subsequent soil penetrations. All soil penetrations occurred in a homogeneous silt deposit. Results are shown in Figure 3.

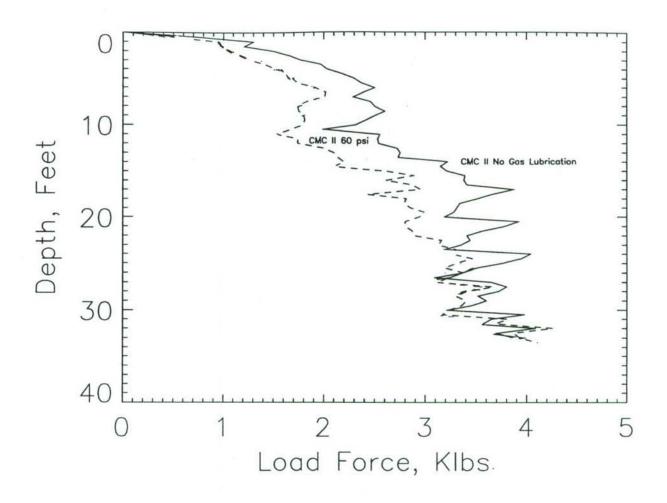


Figure 3. Air Injection Probe Initial Results.

After initial tests were conducted, modifications were made to the air injection probe. Plugging of the small diameter air holes indicated a need for improvement, and an auxiliary method to further reduce circumferential friction was explored. The first attempt at reducing friction consisted of machining a reduced diameter at the air hole location, but plugging of the air holes persisted. Further improvement was obtained by machining an extender at the air hole location, and covering the air holes with an expandable 0-ring. Figure 4 shows the two improved air injection probe configurations.

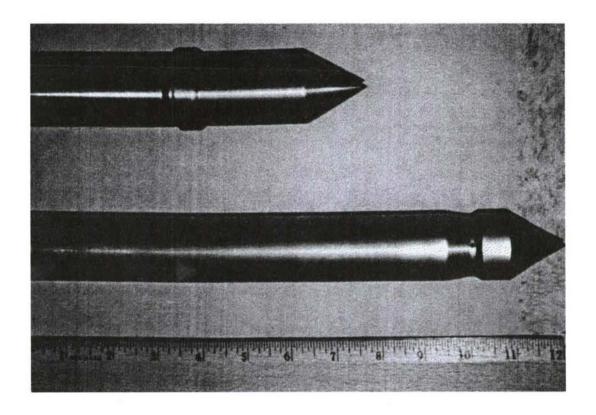


Figure 4. Improved Configurations of the Air Injection Probe.

Field tests were conducted with the unit having the recessed ports. Results show that enhancing the friction reduction capability appears to significantly decrease the force required to achieve soil penetration.

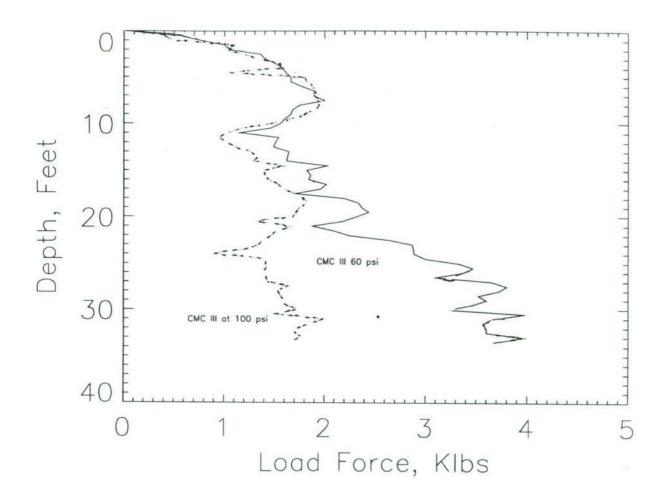


Figure 5. Enhanced Probe Initial Results.

PUSH ROD IMPROVEMENTS

In addition to the air injection probe development, research has been directed in other areas relating to achieving deeper soil penetration with higher resistance to adverse subsurface conditions. Some of these areas include push rod enhancements, angled push capability, and additional sensor development activities.

Push rod enhancements include vacuum-hardening the tool steel and increasing the push rod diameter. Off-the-shelf push rods (commercially available) normally are composed of carbon steel without special hardening. By vacuum-hardening the push rod and probe steel, an outer layer is formed with highly abrasive-resistant and higher yield stress material properties. Such an enhancement not only improves the survivability of the steel material during a soil penetration, but is more economical due to higher longetivity. Particularly susceptible components of the probe are the cone tip and the friction sleeve materials. Hardening these steel components also improves repeatibility of soil penetration strength measurements, as they are subject to less wear and strain softening.

To improve survivability of the push rod during a penetration in which obstacles are encountered, the physical size of the push rod is directly related to its stress capacity. When an obstacle is encountered, there is a tendency for the push rod to skew to the side which imparts bending stresses along the vertical axis. The ability of the push rod to counteract these bending moments is directly related to the cross sectional properties of the steel.

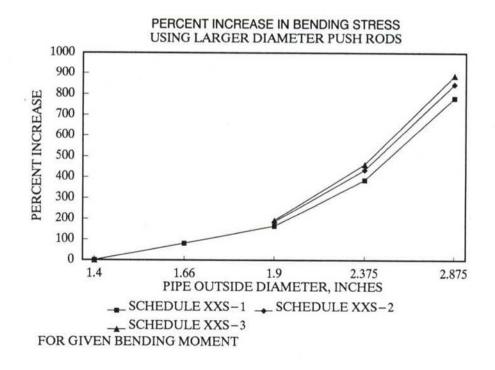


Figure 6. Push rod cross sectional strength considerations



ANGLED PUSH CAPABILITIES

Development of a skid-mounted device capable of angled penetration pushes is ongoing. Such a device is required for locations where a vertical push is not feasible, as under a tank from which a contaminant has leaked. For a variety of technical reasons, it is deemed impractical to simply modify the existing vertical push truck-mounted penetrometer for this special purpose. A skid-mounted device has been modified extensively, and field testing will ensue. This device consists of a hydraulic ram driven by an integral hydraulic pump with support equipment necessary to achieve soil penetration. Approximate dimensions are 213 cm (84 in) wide by 411 cm (162 in) long by 250 cm (98 in) tall, and a weight of 13,200 kg (6000 lb). In addition to vertical pushes, it is capable of pushing at up to 60 degrees from vertical in the angled-push mode. Maximum downward thrust is anticipated to be 178 kN (20 tons) with ballast. Data collection support will be provided externally.

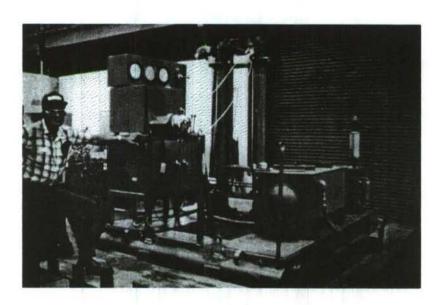


Figure 7. Skid-mounted angled push rig.

Sensor development is also proceeding. Gamma ray scintillation detectors have been purchased and are being modified for incorporation into the penetrometer probe. Data linkage consists of a fiber optic array supplanting the standard electrical signal between the detector and the signal conditioning electronics. Development to incorporate a gamma ray spectral counter package into the penetrometer is underway; a major challenge is management of the physical size constraint and repackaging it into the small diameter penetrometer rod.

CONCLUSIONS AND RECOMMENDATIONS

The SCAPS system has been successfully demonstrated and is considered a valuable tool in the Department of Defense's environmental characterization and remediation efforts. Ongoing and future enhancements to the system will ensure a continued and vital role in the increasingly visible mission of the Department of Defense's research and development responsibilities. Continued field trials will allow incorporation of the enhanced developments with the ultimate goal of transitioning such research and development into fully integrated operational units. Other areas of development which are promising include the following improvements:

- a) Enhanced site support systems, including faster, more accurate, and more integratable field surveying options. Items such as Global Positioning capability and Geographical Information Systems integration will enhance data collection efforts and subsequent reports to sponsors/clients.
- b) Integration of field data collection efforts with data processing and visualization techniques for near real-time presentation to sponsors/clients. Decision-making options will then be readily available.
- c) Robotic capability for operations at hazardous sites, particularly unexploded ordnance areas or extremely toxic sites.
- d) Expansion of traditional cone penetrometer restrictions to areas which are less amenable for penetration. Enhanced capability for operations in such areas (consolidated deposits such as dense clays and shales, and unconsolidated deposits such as gravel layers, cobbles, etc.) will require development of enhanced ballast systems and unique penetration techniques such as air-assisted injection and vibration methods. Hand-in-hand with increased capability in un-amenable deposits is increased depth capability in traditional cone penetrometer applications in sand, silt, and clay deposits.
- e) Improved sampling capability via development of multi-port systems and other hardware improvements.
- f) Development and improvement of detection sensors for screening and quantification of subsurface contaminants; specifically heavy metals, volatile organics, explosives products, and radionuclides.
- g) Incorporation of traditional geophysical downhole logging technologies into the penetrometer. Such capabilities include density and porosity measurement systems and electrical conductivity methods (spontaneous potential, magnetometers, etc.).
- h) Research and development of soil and groundwater parameter measurement systems, including moisture content, saturation limits, vadose zone and saturated zone hydraulic conductivity measurements, and enhanced soil classification methods. Some of this research and development effort will involve incorporation of presently-available systems into the penetrometer, yielding a real-time method of economical and accurate in-situ subsurface characterization; however, most of the effort will entail research and development into areas as yet uncharted for in-situ characterization.

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THE ENVIRONMENTAL RESTORATION RESEARCH, DEVELOPMENT, DEMONSTRATION, TESTING, AND EVALUATION PROGRAM OF THE U.S. DEPARTMENT OF ENERGY OFFICE OF TECHNOLOGY DEVELOPMENT

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ABSTRACT

The U.S. Department of Energy (DOE), Office of Environmental Restoration and Waste Management (EM), Office of Technology Development (OTD) is conducting a research, development, demonstration, testing and evaluation (RDDT&E) program to make available new technologies to achieve compliance with cleanup and waste management requirements at DOE sites. DOE manages the nation's nuclear weapons complex with its unique cleanup and waste management needs, which involve combinations of hazardous and radioactive materials and mixed wastes. In many cases these wastes cannot achieve compliance using currently available technologies, or costs of achieving compliance are extremely expensive. The OTD RDDT&E program is organized in three areas: (1) soil and groundwater cleanup, (2) waste retrieval and processing, and (3) waste minimization. Interagency cooperation with the U.S. Army, Air Force, Navy, and other federal agencies is DOE's principal means of addressing mutual environmental technology needs in a cost-effective manner.

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1. INTRODUCTION

The U.S. Department of Energy (DOE) is committed to bringing its facilities and associated waste sites into compliance with national environmental laws within the next 30 years. This commitment will be accomplished through DOE's Environmental Restoration and Waste Management (EM). EM is responsible for the management of waste from past, present, and future DOE nuclear programs and for DOE sites that generate these wastes. The environmental problems are far ranging in technical scope and geographical distribution. Technical operations include addressing wastes generated during the past years of operation as well as current production at operating facilities. The wastes include radioactive materials, hazardous chemicals, and mixtures of both; these wastes are at DOE sites in more than 30 states. The Office of Technology Development Programs (TD) within EM is responsible for developing innovative environmental restoration technology through research, development, demonstration, testing, and evaluation (RDDT&E) that focuses on solving waste problems common to most DOE sites. To reach the 30-year goal, EM needs new and innovative technologies that achieve waste remediation in a faster, cheaper, better, and safer manner than those currently available. The concept of an integrated demonstration was developed to expedite demonstration of these innovative technologies. The integrated program concept addresses specific technology areas to provide focused research and development (R&D).

2. INTEGRATED DEMONSTRATIONS AND INTEGRATED PROGRAMS

An integrated demonstration is a time- and cost-effective management concept; through a multidimensional approach, interactive technologies for solving environmental restoration and waste management problems are assembled and evaluated at a common waste site to demonstrate a cost-effective system to clean up the problem. An integrated demonstration can be described in three dimensions: technology filtering, operations, and technology integration. The technology filter dimension provides a technology assessment process that allows selection of the most promising new technologies from the innovative technology program; from the applied R&D program; and from technologies of industry, other governmental agencies, and foreign countries for each functional step of the operation. The operations dimension represents functional programmatic steps necessary to solve an environmental cleanup problem end to end (i.e., from characterization through final monitoring for environmental restoration). During the integrated demonstration, a systems approach is used to ensure efficiency, completeness, and compatibility with each step's operational requirements. The technology integration dimension facilitates the

public's and regulatory bodies' quick acceptance of new environmental restoration technologies by interactions with concerned individuals and organizations, and encourages industrial participation to ensure that capabilities to provide the needed remediation services are available.

An integrated program is a set of technical activities dedicated to meeting the needs for technology solutions for a single problem category (e.g., characterization, treatment, minimization, etc.) common to environmental management activities across the DOE complex. Integrated programs focus the development of a technical base for environmental technologies and are centrally managed, though not necessarily centrally located.

RDDT&E projects have been divided into three major areas: (1) Groundwater and Soils Cleanup, (2) Waste Retrieval and Waste Processing, and (3) Waste Minimization. Integrated demonstrations to investigate the priority issues of each area are ongoing, being initiated, or being planned at various DOE sites. Several integrated demonstrations and integrated programs in the groundwater and soils cleanup area and in the waste retrieval and waste processing area will be described to illustrate how an integrated demonstration functions.

2.1 GROUNDWATER AND SOILS CLEANUP

Contamination of soils and groundwater is one of DOE's most pervasive environmental restoration challenges. In the Eastern United States, where rainfall is more abundant than in the west, the precipitation has transported organic, radioactive, and heavy metal waste elements, causing contamination of the soil and of the groundwater usually found close to the land surface. The comparative aridity of the Western United States may reduce transport by the water mechanism there; however, wind erosion and unsaturated vapor transport pose equally challenging cleanup situations.

The integrated demonstrations organized in this category of environmental restoration are mobilized by the need to demonstrate cost-efficient, achievable means of cleaning up vast areas of contaminated soil and groundwater in the DOE weapons complex. The overall objective is to validate cleanup technologies for DOE implementation by demonstrating their effectiveness, cost savings ability, risk-reduction potential, and ability to reduce waste generation and improve DOE's capabilities to meet commitments, consistent with regulatory requirements and public acceptance.

The integrated demonstrations being implemented now are (1) Cleanup of Volatile Organics in Nonarid Soils and Groundwater, (2) Cleanup of Volatile Organics in Arid Soils and Groundwater, (3) Cleanup of Plutonium-Contaminated Surface Soils (arid site), and (4) Cleanup of Uranium-Contaminated Soils (nonarid site), and (5) cleanup of a mixed waste landfill (and site). The progress differs for each demonstration, depending upon its stage of development.

2.1.1 Cleanup of Volatile Organics in Nonarid Soils and Groundwater

This integrated demonstration was DOE's first. Planning of the demonstration was coordinated through the DOE Savannah River Field Office and began in October 1989. The initial objectives of this demonstration are to (1) develop, demonstrate, and compare technologies for remediation of volatile organics [e.g., trichloroethylene (TCE) and tetrachloroethylene (PCE)] in soils and groundwater; (2) span the cradle-to-grave requirements (e.g., from characterization and remediation to closure and monitoring); and (3) develop an integrated demonstration protocol as a basis for planning future integrated demonstrations. Directional drilling techniques

(horizontal wells) are being used as are physical, chemical, and biological remediation technologies. This integrated demonstration also provides for the evaluation of an array of newly developed characterization and monitoring methods from across the DOE complex and private industry.

The remediation of volatile organics is one of DOE's top environmental issues. Implementating new technologies for remediation, characterization, and monitoring should result in large cost reductions. Development costs can also be reduced by the integrated demonstration approach. The in situ cleanup technologies being developed for solvent contamination have applicability at other major DOE sites. Additionally, the characterization and monitoring technologies (e.g., fiber-optic sensors and the cone penetrometer) can be used at many sites and may significantly reduce the costs of analytical sampling and monitoring well construction.

Directional drilling is being demonstrated as a tool to improve access to the subsurface for characterization, monitoring, and remediation. Access under existing facilities can only be acquired using directional drilling. Existing technologies from other industries are being modified and hybridized for environmental applications.

Characterization technologies already demonstrated include depth discrete soil and groundwater sampling, cone penetrometer with real-time analytical capabilities, and nucleic acid probes for microbial characterization.

Monitoring technologies demonstrated include geophysical tomography, fluid-flow sensors, fiber-optic chemical sensors, real-time field analytical methods, multilevel vadose zone, and groundwater samplers.

Remediation technologies include in situ air stripping (air sparging), in situ bioremediation, radio frequency heating, and off-gas treatment technologies such as photocatalytic oxidation, catalytic oxidation, biotreatment, ion beam oxidation, steam reforming, membrane separation, and ultraviolet oxidation.

The biodegradation process has three phases: (1) use of pump-and-treat bioreactors to degrade TCE and PCE in groundwater, (2) use of vegetation to encourage a rhizosphere that can degrade TCE and PCE in surface soil, and (3) use of horizontal wells and methane injection to stimulate in situ biodegradation of TCE. Phase 1 has three parts: isolating microbes that are capable of degrading TCE and PCE in water from TCE-contaminated soil; optimizing the degradation capabilities of these microbes in laboratory bioreactors; and building and testing a pilot-scale (10 gal/min) bioreactor at C&P Burning Rubble Pits.

One benefit from this task is that large-scale bioreactors can be used in various pump-andtreat scenarios for treatment of groundwater to remove both TCE and other volatile and nonvolatile organics.

The testing of Phase 1 processes has been completed at DOE's Savannah River Site (SRS). The results from these tests were positive:

- Bacteria that can aerobically degrade TCE were isolated from native soil;
- Propane or methane was found to stimulate TCE degradation more than several other electron donors;



- Fluidized expanded bed bioreactors, using propane or methane as a primary energy source, were 99 and 50% efficient in reducing TCE concentrations in water, respectively; and
- Other wastes were also degraded when mixed wastes were used in the reactor.

Phase 2 processes were recently tested at SRS. The initial results from this task were positive:

- Vegetated soil was demonstrated to oxidize TCE-contaminated soil faster than unvegetated soil or sterilized soil at the Miscellaneous Chemical Basin;
- Vegetation analysis showed no difference compared with normal vegetation succession for the area;
- Four of the dominant plants at the test site were compared and found to have significantly different abilities to encourage TCE degradation; and
- Phospholipid fatty acid analysis of the rhizosphere defined the physiological state of rhizosphere microbes.

The testing of Phase 3 processes was recently initiated at SRS. The preliminary results from this task and the current status follow:

- Extensive pretest site characterization was completed. The hydrogeology and the contaminant, plume, and indigenous microbial populations were defined;
- An indigenous aerobic microbial population with TCE degradative capacity was identified at the site;
- Populations of TCE degraders increased during the air-only injection campaign;
- Air/methane injection has recently been initiated at the demonstration site.

2.1.2 Cleanup of Volatile Organics in Arid Soils and Groundwater

This integrated demonstration is conducted through the DOE Richland Field Office at a Hanford carbon tetrachloride (CCl₄) release site. The object of this integrated demonstration is to develop and compare technologies for the characterization, removal, and destruction of volatile organic constituents (e.g., CCl₄, TCE, and PCE) at arid sites. Development and field validation of control and performance prediction methods applicable to arid climates or locales with large vadose zones are also vital considerations in the conduct of the integrated demonstration activities.

Additionally, in keeping with the integrated demonstration philosophy, the experience and lessons learned from the SRS nonarid site demonstration will be used. The integrated demonstration is expected to encompass all phases of remedial action, from site characterization and preliminary assessment through remediation to evaluation of effectiveness and monitoring. Control and performance prediction methods must be applicable to arid zones or environments with large vadose zones. The integrated demonstration will survey and evaluate physical, chemical, thermal, biological, electrical, and mechanical technologies for characterization, remediation, and monitoring of contaminated soils and groundwater in arid environments. All

regulatory and permitting requirements will be addressed as a prime segment of the demonstration.

The test site consists of about 7 square miles of semiarid terrain. The test location contains primarily CCl₄, chloroform, and a variety of associated mixed waste contaminants. About 1000 metric tons of CCl₄ were discharged at waste disposal cribs between 1955 and 1973. Chemical processes to recover and purify plutonium at Hanford's plutonium finishing plant resulted in the production of actinide-bearing waste liquid. Both aqueous and organic liquid wastes were generated and routinely discharged to subsurface disposal facilities. The primary radionuclide in the waste streams was plutonium, and the primary organic was CCl₄.

The technologies involved in this Integrated Demonstration include steam reforming, supported liquid membrane separation, membrane separation, in situ bioremediation, in situ heating, in situ corona destruction, development of field screening and real-time measurement capability, and enhanced drilling such as sonic drilling.

Characterization technologies will concentrate on reducing costs and schedules for sampling and analysis and reducing disturbance of the sites. Remediation technologies will concentrate on the degradation of organics to innocuous commodities such as carbon dioxide and water, elimination or reduction to permissible limits of chemical toxicity, extraction of chemical constituents for treatment, and stabilization and segregation of the contaminants from the biosphere. Remediation techniques will focus on reducing costs without creating ancillary waste streams. This demonstration is being held because of DOE's high level of concern for the environmental restoration of soil and groundwater contaminated with organic solvents. Benefits of the demonstration arise from the applicability of these new technologies to priority cleanup needs at Richland, Idaho National Engineering Laboratory (INEL), Los Alamos National Laboratory, Pantex, Rocky Flats Plant (RFP), Lawrence Livermore National Laboratory, Sandia National Laboratories, other DOE sites, and other federal agencies [e.g., the National Aeronautics and Space Administration, Department of Defense (DOD)].

2.1.3 Cleanup of Plutonium-Contaminated Surface Soil

This integrated demonstration is initially focused on restoring one of the nuclear weapons safety shot sites within the Nevada Test Site (NTS). Safety shot sites are typically contaminated on the surface with plutonium or uranium or both; typically 90 to 95% of the contamination resides in the top 5 cm of soil. In the cleanup operation, soil and vegetation will be removed selectively using techniques that reduce the volume of contaminated materials to be removed by possibly placing the coarser uncontaminated particles back on the original surface to serve as a protective cover, preventing wind erosion of the newly exposed surface. Revegetating the site to rehabilitate the fragile ecology of desert ecosystems will be studied. A gravimetric separation process was developed and tested at Johnston Atoll; the process achieved a 95 to 98% volume reduction of plutonium-contaminated coral. Pilot equipment is now at NTS and is available for further evaluation and potential modification.

Other techniques, such as wet screening, magnetic separation, centrifugation, or hydrocycloning, may be evaluated depending on the soil type and the plutonium's physical characteristics. Limited studies of nuclear shots in NTS have shown that plutonium contamination is present in certain size fractions, mainly as fine plutonium oxide particles. At RFP, investigations have shown that the plutonium, although occurring as fine particles in the waste, has chemically aggregated into much larger granules than the initial particle sizes. Soil samples

from RFP, Hanford, Fernald, and other DOE sites are to be examined at NTS for separation efficiency using various techniques. The Environmental Protection Agency is assisting in the evaluation of the soil samples through the National Air and Radiation Environmental Laboratory.

The contaminated soil particles removed from the surface and concentrated must be disposed of in a way that will not create a new potentially hazardous site. Regulatory requirements will dictate the specific method to be used. While traditional methods, including cementation and impermeable cover, are being considered, advance techniques such as vitrification will also be explored.

One of the more difficult challenges may be restoring the cleaned site to its original ecosystem. Restoring vegetation to the soil in a harsh environment, with limited water and without the original surface, requires careful management. Removal of the surface soil exposes the less productive subsoil; the subsoil remaining is less permeable to water than the original surface, making the soil subject to erosion and compaction. In addition, young vegetation attracts wildlife, such as rabbits, and plants can be stripped of their tender leaves during the active growing season. EM is reviewing studies that have provided valuable information on the requirements for revegetation; effective methods to improve water infiltration, such as returning the coarse noncontaminated particles to the surface; and surface soil treatment to improve plant growth potentials.

All cleanup efforts must be followed with the deployment of a reliable monitoring system to establish successful remediation. The type of system used will depend on the requirements for cleanup levels and the techniques used. Thus, the combined and coordinated efforts of characterization, cleanup with volume reduction, ultimate disposal of the contaminants, restoration of the site to a sound ecologic system, and documentation of the safe long-term cleanup of the contaminated site typify the integrated demonstration concept.

2.1.4 Cleanup of Uranium-Contaminated Soil

The objective of this integrated demonstration is to develop and demonstrate remediation methods for soils contaminated with uranium. The DOE Oak Ridge Field Office is coordinating the demonstration. Remediation techniques for cleaning up large areas contaminated with uranium will be evaluated for removal efficiency, economic feasibility, risk reduction, and waste minimization. Traditional methods for remediating radionuclide-contaminated soils, such as excavation, transportation, and permanent storage, are costly (estimates have been formulated of approximately \$700 or greater/yd³ depending on site and conditions) because of the large volumes of soil to be removed. The demonstration will span the cradle-to-grave phases involved in an actual cleanup, addressing all regulatory and permitting requirements and expediting future selection and implementation of the most appropriate technologies, in terms of immediate and long-term effectiveness, for all DOE sites. The demonstration will complement the demonstration for plutonium contamination that the DOE Nevada Field Office is conducting at NTS.

The Fernald Environmental Management Project (FEMP) location in Ohio is the site for the integrated demonstration of cleanup of uranium-contaminated soils because of its off-site contamination and because the state of Ohio's concerns are very pressing. [This facility was formally named the Feed Materials Production Center (FMPC).] Additionally, remediation technology information derived from the demonstration will be beneficial and may be transferred to the Oak Ridge, Portsmouth, Paducah, Idaho, Savannah River, and Richland sites for cleanup

of radionuclide-contaminated soils. The primary problem at FMPC is that radioactive soil contamination, predominantly depleted uranium, is widespread.

The prospective demonstration site at FEMP is an area of contaminated soils adjacent to the solid waste incinerator, which is at the northwest corner of the sewage treatment plant. The incinerator was operated from November 1954 through December 1979 and was used to burn contaminated and uncontaminated burnable trash. Remediation for this site is important, because most of the contaminated soils are outside the fenced boundary of the sewage treatment plant, and a neighboring farmer has used the site through a lease agreement with DOE (i.e., DOEowned land) to graze cattle. Remedial Investigation /Feasibility Study soil and core sampling data were collected; the highest concentrations of uranium were in the immediate vicinity of the incinerator, and the apparent plume extended toward the northeast, which is the most probable wind direction. Limited data from core samples for this area, down to 7 ft, show that uranium can penetrate the soil and may be adsorbed to the clay in the soils. The data also suggested that in some areas no remediation is necessary; other samples showed that remediation may be necessary in some areas down to 1 ft and in other areas down to 5 ft (probably because of fissure flow). In addition, physical cleanup techniques that may work in arid, sandy soils may not work well in the fine, clay soils at the FEMP site; the uranium is chemically exchanged on the soil at FEMP and does not appear in the discrete plutonium particles found at the Nevada plutonium demonstration site. FEMP will send soil samples to Nevada to determine the effectiveness of a gravimetric separation process (AWC process) for remediation of FMPC soils. Remediation techniques based on chemical removal (extraction) or desorbing radionuclides (uranium) from the soils may be required.

2.1.5 Mixed Waste Landfill (Sandia)

The objective of this integrated demonstration is to develop, demonstrate, and compare technologies for the characterization and remediation of organic/inorganic (mixed waste) vadose zone landfills and contents. The demonstration will cover all phases involved in an actual cleanup (including all regulatory and permitting requirements), expedite future selections, and implement the best technologies to show immediate and long-term effectiveness for all DOE sites. The first phase of the integrated demonstration (ID) will involve the characterization and remediation of a Chemical Waste Landfill (CWL), that contains a combination of acids, oxidizers, reducers, organics, alkaline metals, alkaline earths, and heavy metals. The second phase involved the characterization and remediation of a Mixed Waste Landfill (MWL), that contains transuranic waste, uranium/thorium waste, fission products, induced-activity materials, and tritium-containing waste. The ID for the CWL and MWL will be developed in accordance with OTD's model and will involve all technical and regulatory activities necessary to remediate and close the sites. This will include site characterization, remediation, performance assessment, secondary waste treatment, and postclosure monitoring, as required.

2.1.6 In Situ Remediation

The In Situ Remediation Integrated Program will emphasize the development of on-site treatment technologies at the pilot-plant scale and evaluate for technical feasibility, economic attractiveness, and regulatory acceptability. In situ remedial technology minimizes environmental disruption, reduces landform dislocations, reduces cost of restoration, minimizes personnel exposure to hazardous and radioactive contaminants, and limits secondary waste stream generation. In situ remediation technology involves bioremediation using microbes to destroy hazardous organics such as TCE, leaching and soil washing methods to destroy waste without

excavation, and biofiltration, which uses microbes strategically placed to prevent further transport through decomposition of hazardous organics. As a corollary to investigations with microbes in subsurface media, considerations of soil surface conditions to optimize microorganism populations to destroy hazardous organics are included. By comparing technologies under varying conditions based on site characteristics, the best treatments would be selected for application at different sites to remediate noxious conditions.

2.1.7 Characterization and Sensor Technology

The Characterization and Sensor Technology Integrated Program will involve characterization and sensor technology at the pilot-plant scale and evaluation for technical feasibility, economic attractiveness, and regulatory acceptance. This integrated program will minimize ER/EM costs by avoiding redundant sampling. Characterization and Sensor Technology involves a spectrum of chemical and physical measurements to analyze inorganic and organic contaminants in waste containers as well as those in soils and groundwater at DOE sites. The technologies will guide selection of proper cost-effective waste remediation and avoid redundant and excessive samplings. Approaches under development include rapid, inexpensive, reliable, real-time, on-site, portable, remote sampling/remote sensing, nondestructive, nonintrusive features; advantages include cost reduction, rapid and timely analysis, minimal storage, and reduced environmental risks. By evaluating technologies under varying conditions based on site characteristics, the best techniques would be selected for application to different sites.

2.2 WASTE RETRIEVAL AND WASTE PROCESSING

In response to environmental mandates, waste retrieval and waste processing technologies will be developed and advanced through integrated demonstrations and other demonstrations that involve the following: (1) excavation or removal of contaminated material from the site or tank by remote or direct contact techniques, (2) treatment and disposal of retrieved waste or waste arising from operations, (3) processing of contaminated material into a suitable form for shipping and/or disposal, or (4) decontamination of materials and equipment and decommissioning of facilities. These technologies will minimize the toxicity and volume of waste; accomplish faster, better, cheaper, and safer remediation of waste problems; and produce waste within regulatory guidelines for safe, permanent disposal.

A number of integrated demonstrations and integrated programs are under way or in the planning stages. They include buried waste, underground storage tanks, newly generated mixed waste, weapons component waste disposal, in situ vitrification, decontamination and decommissioning of metal and concrete structures and materials, and advanced processing. Each integrated demonstration will use discriminating cradle-to-grave considerations to assemble, test, and evaluate related and synergistic technologies. These considerations will define an integrated system based on prototypic performance, safety, costs, and regulatory and social acceptability to remediate or manage DOE's environmental and waste management programs.

2.2.1 Buried Waste Integrated Demonstration

The buried waste integrated demonstration will focus on buried transuranic waste at INEL; coordination of this demonstration is by the DOE Idaho Falls Field Office. The objective of this integrated demonstration will be to compare an array of technologies for in situ remediation and retrieval, separation and concentration, treatment, and disposal of mixed wastes from buried waste

sites. The approach will span all phases involved in an actual cleanup and allow comparison of the technical performance of different available technologies under actual field conditions for potential use at other DOE facilities. Specifically, treatment technologies for radionuclides, toxic metals, and organic contaminants on rags, laboratory glassware, used test equipment, and other trash materials will be evaluated. Processing techniques to separate contaminants will also be demonstrated. The project is based on the need for improved separation and concentration technologies to separate mixed waste into its radioactive and hazardous components, allowing treatment and disposal consistent with EPA/NRC below regulatory control standards. The program is designed to contribute to meeting The DOE/Idaho State commitments for site remediation. Additional benefits include technology transfers to the Hanford, Los Alamos, Rocky Flats, Oak Ridge, and Savannah River installations.

2.2.2 Underground Storage Tanks Integrated Demonstration

The technologies developed in the Underground Storage Tanks Integrated Demonstration (UST-ID) Program will be used in remediation actions at five participating DOE sites: Hanford (the host site), Fernald, Idaho, Oak Ridge, and Savannah River.

These five sites began operations between 1943 and the early 1950s. They originally supported nuclear fuels production, operations, and research programs as part of the development of nuclear weapons started during and subsequent to World War II. Most of the site missions have evolved from production to peaceful uses of nuclear power, research and development, and environmental cleanup.

A variety of processes were used to produce nuclear fuels (enriched uranium, plutonium, and tritium production and recovery process) at these sites. Most of the radioactive liquid waste currently contained in the underground tanks was generated by the chemical processes used to separate nuclear fuels from other components. Early separation processes generated large quantities of waste (117,000 gal/ton of product). Modern processes were designed to minimize waste; most generate relatively small quantities of waste (300 gal/ton of product).

The major emphasis of this ID is the 149 single-shell storage tanks located at the Hanford Site. The Hanford Site is located in the southeastern section of Washington State near the cities of Richland, Kennewick, and Pasco. It has operated since 1943, with a primary mission of producing plutonium isotopes. Plutonium was produced by irradiation of enriched uranium in eight nuclear reactors located along the Columbia River. The plutonium was separated from the remaining uranium and fission products by chemical processes. It was then sent off site for further purification.

The UST-ID was created in February 1991 to develop unique state-of-the-art and advanced state-of-the-art technologies that can be applied to ongoing and planned environmental programs at sites across the DOE complex. The UST-ID is necessary to enable a final decision on disposal of UST wastes and soils, groundwater, and ancillary equipment. Six technical focus areas have been formed under the UST-ID:

- 1. Characterization;
- 2. Retrieval, transfer, and storage;
- 3. Waste separation;
- 4. High- and low-level waste treatment;



- 5. In situ treatment and disposal; and
- 6. Site closure.

Currently, the UST-ID Program emphasizes technologies that provide near-term benefits toward remediation of USTs. This approach will garner end-user program support and foster synergy between the UST-ID Program and the end-user programs. FY 1992 efforts are directed toward the first three areas, which are shared by most of the participant sites. (Smaller investments are dedicated to the remaining focus areas, but these areas are nonetheless critical.)

Characterization of tank wastes has traditionally been limited by high analytical costs and the inability to obtain data from many points in the tanks. Hence, tasks have been selected to develop sensors that will decrease laboratory analytical time and a means for deploying these sensors inside the tank. Laser Raman spectroscopic sensors being developed will first be used in the analytical laboratory and, when proven, will be configured for in-tank use.

Waste retrieval techniques will be tested using a light-duty utility arm. Designed for in situ deployment, this articulated, remotely operated arm will deploy characterization devices and test some features of waste retrieval technology on actual tank waste. It is expected that this arm will be able to deliver characterization tools, such as optical sensors and physical measurement devices, to obtain data of much higher statistical certainty than is currently possible.

2.3 WASTE MINIMIZATION

Waste minimization activities focus on reducing the generation of hazardous waste during all phases of site remediation activities, waste processing activities, and during the production of weapons. Primarily, the major activities currently are associated with the substitution for halogenated solvents and the application of advanced manufacturing techniques to reduce the amount of metal waste produced. The following describes some of the ongoing waste minimization efforts within OTD.

2.3.1 Environmentally Conscious Electronic Manufacturing

The Environmentally Conscious Electronic Manufacturing Integrated Demonstration is designed to meet the Montreal Protocol (international requirement to reduce air emissions of chlorinated hydrocarbons), to reduce risk to production workers, and to reduce the cost of electronics production. The demonstration covers all phases involved in processing. It involves all regulatory and permitting requirements, expediting future selection and implementation of the best technologies to show immediate and long-term effectiveness for all DOE sites. The demonstration provides for technical performance comparisons of different available technologies based on cost effectiveness, risk reduction effectiveness, technology effectiveness, and general acceptability. Specifically, the demonstration will address "dry process" cleaning, fluxless soldering, waster soluble degreasers and machine coolants, dry machining, solvent substitution, liquid CO₂ cleaning, argon cleaning, VOC abatement, and conductive adhesives.

2.3.2 DOE/Air Force Memorandum of Agreement

The DOE/Air Force MOA Integrated Demonstration will develop material substitution and advanced manufacturing techniques to reduce or eliminate hazardous waste. This demonstration shows that DOE and the Air Force are actively working to reduce waste production. Joint

Agency solutions to shared problems, including substitution of chlorinated solvents and metal manufacturing process development, leverages DOE funds. The demonstration covers all phases involved in processing. It includes all regulatory and permitting requirements, expediting future selection and implementation of the best technologies to show immediate and long-term effectiveness for all DOE sites. The demonstration provides for technical performance comparisons of different available technologies, based on cost effectiveness, risk reduction effectiveness, technology effectiveness, and general acceptability. Specifically, the demonstration will address alternative cleaning processes, solvent substitution, and metal manufacturing technologies. Also, management and disposal of chemicals used in metal cutting, forming and coating operations are an increasingly difficult problem. DOE's goal is to develop environmentally compliant manufacturing technology through technology exchange.

2.3.3 DP/EM Memorandum of Understanding

This integrated demonstration will show that DOE/DP/EM are actively working to reduce waste production because 80% of DOE's waste is generated in nuclear weapons complexes. The demonstration covers all phases involved in processing. It includes all regulatory and permitting requirements, expediting future selection and implementation of the best technologies to show immediate and long-term effectiveness for all DOE sites. Specifically, the demonstration will address process line modeling, product design, and process line changes to reduce waste, and the implementation of solvent substitution technology developed elsewhere.

3.0 INTERAGENCY COOPERATION

Where areas of mutual interest exist, cooperative agreements with other agencies of the government are explored. Duplication of research and demonstration efforts is avoided and maximum use of budgeting assets is achieved. Some examples of interagency cooperation are listed.

3.1 DEPARTMENT OF ENERGY/AIR FORCE MEMORANDUM OF AGREEMENT

(This project was previously described in Section 2.3.2 and is included here as an example of interagency cooperation.)

3.2 DEPARTMENT OF ENERGY/ARMY INTERAGENCY AGREEMENT FOR SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM RESEARCH, DEVELOPMENT, AND DEMONSTRATION

DOE's mission has produced a variety of situations where there is a high probability of soil and groundwater contamination with both industrial and radiological wastes. Within the DOD, the U.S. Army Toxic and Hazardous Materials Agency has tasked the U.S. Army Corps of Engineers Waterways Experiment Station (WES) to the development of cone penetrometer equipment for conventional hazardous wastes, including explosives (first priority for the Army), solvents, metals, and hydrocarbons (petroleum, oil, and lubricants). The WES is actively pursuing research with the Naval Ocean Systems Center (NOSC) and the Air Force Civil Engineering Support Agency (AFCESA) to address these needs. The NOSC and AFCESA research programs provide state-of-the-art expertise in remote fiber-optic fluorescence measurements with laser

excitation, while the WES contribution includes design, fabrication, and implementation of cone penetrometer sensors and samplers. The truck and associated contaminant and hydrologic sensor systems developed in this research effort is called the Site Characterization and Analysis Penetrometer System (SCAPS).

These capabilities can also be used to advantage in developing special purpose technologies to suit DOE needs. The current joint DOD/DOE effort will strengthen the development process, accelerate delivery of field-proven products by pooling resources, and provide innovative equipment at less cost to each participating agency. To provide the DOE with rapid and cost-effective means to accomplish site characterization and assessment actions, the WES is assisting DOE in six major activities, as follows:

Activity 1. Construction of a penetrometer truck for DOE for use on hazardous and mixed waste contaminated sites.

Activity 2. Conduct field demonstration tests at DOE sites. The WES is performing field demonstrations of the DOE penetrometer equipment at a DOE site or sites in each year of the program. Each demonstration requires 3 to 4 weeks and serves primarily to field-test products of the development process. Secondary objectives are to provide data for input to remediation action planning and to provide opportunities for technology transfer and training.

Activity 3. Adapt contaminant sensors for penetrometer use. Common interests among DOE and DOE organizations include the detection of classes of conventional wastes such as solvents, metals, and petroleum, oil, and lubricants. In addition, the Army has a special interest in explosives detection and DOE has the requirement to detect radiological contaminants in situ.

Activity 4. Develop fluid soil sampler. Commercial samplers have proven to be useable, but all units had structural failures in testing at depths ranging from 20 to 100 ft; no samplers have grouting capability (nor could they easily be engineered to provide this capability). Therefore, the WES will design, fabricate, and demonstrate a single soil sampling device with improved overall structural strength, improved lock function during sampling (a persistent problem with conventional designs), and a two-component grouting capability to seal the hose as the sampler is withdrawn. Also, a dependable, single-fluid-sampling device with grouting capabilities will be designed, fabricated, and demonstrated. In addition, a sampler will be developed for taking multiple discrete samples during a single push (three high-quality samples, minimum) with grouting on withdrawal.

Activity 5. Development of angled push capability. The WES will develop a skid-mounted device capable of angled pushes (i.e., under tanks or other structures where vertical pushes are not favorable). For a variety of technical reasons, it is impractical to modify a vertical push truck-mounted penetrometer for this special purpose; however, the WES has a skid-mounted push rig that could be used to evaluate the practicality and utility of such a system.

Activity 6. If requested, conduct training of a DOE or DOE-contractor crew for operation of the SCAPS at DOE sites.

4. COMMENTS

These integrated demonstration and integrated program activities will transfer new and improved waste remediation, waste retrieval, and waste processing technologies to Environmental Restoration, Waste Operations, and Defense Programs where they will minimize the toxicity and volume of waste; manage unavoidable waste more efficiently and safely; accomplish faster, better, cheaper, and safer remediation of waste problems; effectively decontaminate materials and facilities; and produce waste within regulatory guidelines for safe, permanent disposal. New cleanup and waste management technologies must be continually developed, demonstrated, and implemented to achieve and maintain complete regulatory compliance.

TECHNOLOGY DEMONSTRATION THROUGH THE SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION (SITE) PROGRAM

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ABSTRACT

The Superfund Innovative Technology Evaluation (SITE) Program is in its seventh year of developing and evaluating new technologies which may contribute to the cleanup of hazardous waste sites. The SITE Program is composed of an Emerging Technology Program, a Demonstration Program, a Monitoring and Measurement Technologies Program, and a Technology Transfer Program. Field evaluations of the Demonstration Program concentrate on producing reliable engineering, performance, and cost information about specific technologies. The current Demonstration Program contains eightyeight technologies. Thirty-five demonstrations, featuring systems for biological treatment, physical/chemical separation and treatment, materials handling, solidification/stabilization, and thermal destruction, have taken place over the past six years. Evaluations within the last twelve months have included Ecova's bioslurry reactor, Dehydro-Tech's Carver-Greenfield Process, Retech's plasma arc vitrification unit, the Babcock and Wilcox cyclone furnace, Weston Services' low temperature thermal treatment unit, the steam injection and vacuum extraction process of Hughes Environmental Systems, Wastech's solidification/stabilization technology, membrane separation by SBP Technologies, soil recycling work by the Toronto Harbor Commissioners, soil washing with the BioGenesis process, Bergmann's soil washing technology, thermal desorption by Chemical Waste Management, and microfiltration with the EPOC Water system. Wastes treated have included refinery sludges, fuels, wood preserving chemicals, metals, and mixed organic compounds, while the demonstration sites have encompassed Superfund sites, Test and Evaluation Facilities, landfills, and military sites. Details of these demonstration projects are presented in the paper along with a general description of the SITE Program.

INTRODUCTION

The Superfund Innovative Technology Evaluation (SITE) Program, now in its seventh year, evaluates new and promising treatment and monitoring technologies for implementation at hazardous waste sites. The program was created to encourage the development and routine use of innovative technologies as an integral part of EPA's research into alternative cleanup methods for hazardous waste sites. Under the SITE Program, EPA enters into cooperative agreements with innovative technology vendors to develop and demonstrate their technologies at hazardous waste sites. (1)

The successful implementation of innovative technologies requires a team approach. SITE personnel work closely with EPA's regional offices, the states, other Federal Agencies, technology developers, the Superfund Technology Assistance Response Teams (START), and EPA's Technology Innovation Office (TIO) in attempting to provide complete and useable technology evaluation documents and video presentations. A goal of the SITE Program is to provide environmental decision makers with evaluations and data on new,

viable treatment technologies that may aid in site remediation.

The SITE Program includes the following component programs:

- Demonstration Program Conducts and evaluates demonstrations of promising innovative technologies to provide reliable engineering, performance, and cost information for future site cleanup decision-making;
- Emerging Technology Program Provides competitive funding for continued research efforts at bench- and pilot-scale levels to promote the development of emerging, innovative technologies;
- Monitoring and Measurement Technologies Program Develops technologies that detect, monitor, and measure hazardous and toxic substances to provide better, faster, and more cost-effective methods for the character and extent of contamination;
- Technology Transfer Program Disseminates technical information on innovative technologies to speed their commercialization and use.

DEMONSTRATION PROGRAM

The Demonstration Program, the largest portion of SITE, has completed 35 demonstrations and has two, long-term, biological treatment processes in the field for the summer of 1992. The scale of demonstrations is flexible in order to accommodate the wide variety of technologies that are expected to join the program, and is determined by the priority to provide data that are acceptable from both the QA/QC and the user community perspectives. The preference, however, is for field-scale, commercial demonstrations.

Technology demonstrations may be conducted at Federal or State Superfund sites (remedial or removal action sites), federal facilities, EPA test and evaluation facilities, private sites, or the vendor's facility. The criteria for selecting a site are established by the Office of Research and Development in conjunction with the technology vendor, the Office of Solid Waste and Emergency Response, and EPA's Regional Offices.

In general, the vendor is required to operate the technology at the selected location. EPA is primarily responsible for the development of the demonstration plan and is fully responsible for all sampling and analytical activities as well as all reporting. The vendor and EPA must agree to the content of the demonstration plan which consists of four major sections: an Operation Plan; a Sampling and Analysis Plan; a QA/QC Plan; and a Health and Safety Plan.

The final products of each demonstration project will generally be two EPA reports; a Technology Evaluation Report and an Applications Analysis Report (AAR). The Technology Evaluation Report presents the results of the technology performance. It includes a description of the technology and its purpose, a presentation of the demonstration plan (including the operational plan, the sampling and analysis procedures, the QA/QC protocol, and the health and safety issues), the test results (with associated QA/QC data), and cost

data. The AAR discusses the applicability of the technology to other waste media, sites, constituents, and concentrations; as well as detail the capital and operating costs. EPA is utilizing a common format for presenting cost information in all SITE reports and these costs include, but are not limited to the following items: operating cost (including a detailed list of types of requirements, and the cost of each); maintenance cost; waste pre-treatment and post-treatment cost, if applicable; and the potential for cost recovery (ability to recycle residues, or process streams, if applicable).

In addition to the EPA reports noted, demonstration results are also presented at technical conferences and/or published as technical papers in journals and symposium proceedings. These reports and papers provide EPA, the States, and the public with performance data on new commercial technologies with solutions to waste site problems, and with specific cost data useful for comparing and selecting on-site cleanup technologies. Other standard technology transfer items coming from a demonstration include the widely-distributed, two-page demonstration bulletin and a short videotape presentation of the demonstration and its results.

RECENT DEMONSTRATIONS

During the past year, thirteen technologies were evaluated in the field. Two demonstrations, EPA's fungal degradation process and Bio-Rem's augmented in situ subsurface bioremediation process, have been initiated in the field and will continue into Fall 1992. The completed technologies are summarized below along with a brief discussion of results of the field performance. (2)

Babcock and Wilcox Co., Alliance, OH. This furnace technology is designed to decontaminate wastes containing both organic and metal contaminants. The cyclone furnace retains heavy metals in a non-leachable slag and vaporizes and incinerates the organic materials in the wastes. The treated soils resemble natural obsidian (volcanic glass), similar to the final product from vitrification. The furnace is a horizontal cylinder and is designed for heat release rates greater than 450,000 British thermal units (Btu) per cubic foot and gas temperatures exceeding 3,000 degrees Fahrenheit Natural gas and preheated primary combustion air (820°F) enter the furnace tangentially. Secondary air (820°F), natural gas, and the soil matrix enter tangentially along the cyclone barrel (secondary air inlet location). The resulting swirling action efficiently mixes air and fuel and increases combustion gas residence time. Dry soil has been tested at pilot-scale feed rates of 50 and 200 pounds per hour (lb/hr). The soil is retained on the furnace wall by centrifugal action; it melts and captures a portion of the heavy metals. The organics are destroyed in the molten slag layer. The slag exits the cyclone furnace (slag temperature at this location is 2,400°F) and is dropped into a water-filled slag tank where it solidifies into a nonleachable vitrified material. A small quantity of the soil also exits as flyash from the furnace and is collected in a baghouse.

Demonstration of the cyclone furnace took place at the Babcock and Wilcox facility in Alliance Ohio during November 1991. A synthetic soil matrix, spiked with heavy metals, semivolatile organics, and radionuclide surrogates, was used for the demonstration. The furnace was fed at a rate of 170 pounds per hour and remediated approximately 3 tons of soil for the entire demonstration period. The slag produced from the furnace complied with

Toxicity Characteristic Leaching Procedure (TCLP) regulatory requirements, and destruction and removal efficiencies for the organics were greater than 99.99 percent.

Bergmann USA, Stafford Springs, CT. Bergmann's sediment soil washing technology separates contaminated particles by grain size and density. The system operates on the theory that most contamination resides in the fine soil particles and that contaminant levels on the larger particles is not extensive. First, the process classifies the soil feed to remove rocks and debris. Water and chemical additives (surfactants, acids, bases, and chelating agents) are then supplied to the feed stream to produce a slurry which flows to the attrition scrubbing machine. Rotating impellers create fluid and mechanical shear stress to separate silts and clays from granular soil particles. Several different separation processes then create output streams of granular particles, fines, and wash water. The technology is suitable for sediments contaminated with polychlorinated biphenyls (PCBs), and has also been applied to soils and sediments containing organics and heavy metals.

Demonstration of the Bergmann sediment soil washing technology took place in May 1992 in the Saginaw Bay of Lake Michigan near Bay City, MI. The separation unit operated on dredge material that had been stockpiled by the US Army Corps of Engineers. The Bergmann equipment ran over an extended period of time with little difficulty. Analytical results from the demonstration are not currently available.

BioGenesis Enterprises, Inc., Fairfax Station, VA. The BioGenesis[™] soil cleaning process uses a specialized truck, water, and a complex surfactant to clean contaminated soil. Ancillary equipment includes gravity oil and water separators, coalescing filters, and a bioreactor. The cleaning rate for oil contamination of 5,000 parts per million (ppm) is about 25 tons/hour; lesser rates apply for more contaminated soil. To begin the soil cleaning process aeration equipment agitates the soil-water-surfactant mixture, thus washing the soil and encapsulating oil molecules with BioGenesis[™] cleaner. After washing, the extracted oil is reclaimed, wash water is recycled or treated, and the soil is dumped from the soil washer. The cleaned soil may be returned to the site or landfilled at a separate location. Hazardous organics, such as PCBs, are extracted in the same manner and then processed by using treatment methods specific to that hazard. All equipment is mobile, and treatment is normally on-site.

This technology is designed for extracting volatile and nonvolatile oils, chlorinated hydrocarbons, pesticides, and other organics from most types of soils, including clays. Contaminants subject to the process include asphalteens, heating oils, diesel fuel, gasoline, PCBs, and polycyclic aromatic hydrocarbons.

The cleaning agent utilized is a slightly alkaline, organic compound that cleans the soil and also accelerates the breakdown of contaminants. When mixed with hydrocarbons or other organics, the BioGenesis* cleaner is reported to stimulate common soil microorganisms to accelerate biodegradation of remaining trace contaminants.



Demonstration of the BioGenesis process was conducted in May 1992 at an

oil-contaminated site in Santa Maria, CA. Soil was excavated from the site (nearly 350 cubic yards) and stockpiled for the evaluation. The equipment performed as specified for the demonstration, and visual inspection indicated that most of the oil had been removed from the soil and reclaimed. Specific analytical results are not currently available, and the treated soil is being stored for analysis of subsequent biological degradation.

Chemical Waste Management, Inc., Geneva, IL. The X*TRAX™ technology is a thermal desorption process designed to remove organic contaminants from soils, sludges, and other solid media. It is not an incinerator nor a pyrolysis system; chemical oxidation reactions are not encouraged, and no combustion by-products are formed. The organic contaminants are removed as a condensed liquid that may be destroyed in a permitted incinerator or used as a supplemental fuel. Because of low operating temperatures (200 to 900 °F) and gas flow rates, this process is less expensive than incineration.

An externally-fired rotary dryer is used to volatilize the water and organic contaminants into an inert carrier gas stream. The processed solids are then cooled with treated condensed water to eliminate dusting. The solids are ready to be placed and compacted in their original location while the organic contaminants and water vapor driven from the solids are transported out of the dryer by nitrogen carrier gas. The carrier gas flows through a duct to the gas treatment system, where organic vapors, water vapor, and dust particles are removed and recovered. Most of the carrier gas passing through the gas treatment system is reheated and recycled to the dryer.

The process can remove and collect volatiles, semivolatiles, and PCBs, and has been demonstrated on a variety of soils ranging from sand to very cohesive clays. In most cases, volatile organics are reduced to below 1 ppm and frequently to below the laboratory detection level. Semivolatile organics are typically reduced to less than 10 ppm and frequently below 1 ppm.

Demonstration of the $X*TRAX^{\mathbb{N}}$ technology was accomplished during May 1992 at the Resolve Superfund Site in Massachusetts. The unit functioned as specified and analytical data are being generated to verify the cleanup levels attained for the soils. A follow-on demonstration will be held later in 1992 to evaluate dechlorination of the condensed organics by Chemical Waste Management's DeChlor/KGME process.

Dehydro-Tech Corporation, East Hanover, NJ. The Carver-Greenfield Process® is designed to separate materials into their constituent solid, oil (including oil-soluble substances), and water phases. It is intended mainly for soils and sludges contaminated with oil-soluble hazardous compounds. The technology uses a food-grade carrier oil to extract the oil-soluble contaminants. The carrier oil, with a boiling point of 400 °F, is typically mixed with waste sludge or soil, and the mixture is placed in an evaporation system to remove any water. The oil serves to fluidize the mix and maintain a low slurry viscosity to ensure efficient heat transfer, allowing virtually all of the water to evaporate. Oil-soluble contaminants are extracted from the waste by the carrier oil. Volatile compounds present in the waste are also stripped in this step and condensed with the carrier oil or water. After the water is evaporated from the mixture, the resulting dried slurry is sent to a centrifuging section that removes most of the carrier oil and contaminants from the solids. After centrifuging, residual carrier oil is

removed from the solids by a process known as "hydroextraction." The carrier oil is recovered by evaporation and steam stripping. The hazardous constituents are removed from the carrier oil by distillation. This stream can be incinerated or reclaimed. In some cases, heavy metals in the solids will be complexed with hydrocarbons and will also be extracted by the carrier oil.

The demonstration of this technology was completed in August 1991 at EPA's facility in Edison, New Jersey. Petroleum wastes (drilling muds) from the PAB oil site in Abbeville, Louisiana, were used for the demonstration. Results indicate a successful separation of oily drilling muds into their constituent oil, water, and solid phases. No detectable levels of indigenous total petroleum hydrocarbons were found in the solids. Further, metal and organic values were below the TCLP limits for characteristic wastes. Water from the system requires some additional treatment due to the presence of light organics and solvent oil.

ECOVA Corporation, Redmond, WA. ECOVA's slurry-phase bioremediation (bioslurry) technology is designed to biodegrade creosote-contaminated materials by employing aerobic bacteria that use the contaminants as their carbon source. The technology uses batch and continuous flow bioreactors to process polycyclic aromatic hydrocarbon (PAH)-contaminated soils, sediments, and sludges. Because site-specific environments influence biological treatment, all chemical, physical, and microbial factors are designed into the treatment process. The ultimate goal is to convert organic wastes into biomass, relatively harmless byproducts of microbial metabolism, such as carbon dioxide, methane, and inorganic salts.

ECOVA Corporation conducted bench- and pilot-scale process development studies using a slurry phase biotreatment design to evaluate bioremediation of PAHs in creosote contaminated soil collected from the Burlington Northern Superfund site in Brainerd, Minnesota. Bench-scale studies were performed prior to pilot-scale evaluations in order to collect data to determine the optimal treatment protocols. Data obtained from the optimized pilot-scale program will be used to establish treatment standards for KOOl wastes as part of the EPA's Best Demonstrated Available Technology (BDAT) program.

From May through September 1991, EPA conducted a SITE demonstration of the process using six bioslurry reactors at EPA's Test and Evaluation Facility in Cincinnati, Ohio. The reactors processed creosote-contaminated soil taken from the Burlington Northern Superfund site in Brainerd, Minnesota. Results from the pilot-scale bioreactor evaluation showed an initial reduction of 89.3 percent of the total soil-bound PAHs in the first two weeks. An overall reduction of 93.4 percent was seen over a 12-week treatment period.

EPOC Water, Inc. In the first step of this process, heavy metals are chemically precipitated. The precipitates, along with all particles down to 0.1 micron, are filtered through a unique fabric, crossflow microfilter (EXXFLOW). The concentrate stream is then dewatered in an automatic tubular filter press of the same fabric material (EXXPRESS).

EXXFLOW microfilter modules consist of an array of tubes constructed of a proprietary woven polyester. Wastes are pumped into the tubes and the precipitates form a dynamic membrane with any other suspended solids. The

concentrate stream will contain up to 5 percent solids for discharge to the EXXPRESS system. The EXXFLOW concentrate stream enters the EXXPRESS modules with the discharge valve closed. A semi-dry cake, up to 1/4 inch thick, is then formed on the inside of the tubular cloth. When the discharge valve is opened, rollers on the outside of the tube move to form a venturi within the tube. The venturi creates an area of high velocity within the tubes that aggressively cleans the cloth and discharges the cake in chip form onto a wedge wire screen. The discharge water is recycled back to the feed tank. The EXXPRESS filter cakes are typically 40 to 60 percent solids by weight.

The EXXFLOW/EXPRESS demonstration unit is skid-mounted and designed to process approximately 30 pounds of solids per hour and 10 gallons per minute of wastewater. The technology is designed to be applicable to water containing heavy metals, pesticides, oil and grease, bacteria, suspended solids, and constituents that can be precipitated into particle sizes greater than 0.1 micron.

Demonstration of the EPOC Water system took place in May and June 1992 at the Iron Mountain Superfund Site in California. Two separate strengths of acid mine drainage were applied to the system during the test program. After considerable effort to design the precipitation step, the filter seemed to function as designed. Data from the demonstration will be available by Fall 1992.

Hughes Environmental Systems, Inc., Manhattan Beach, CA. The steam injection and vacuum extraction (SIVE) process developed by Hughes Environmental Systems, removes most volatile organic compounds (VOC) and semivolatile organic compounds (SVOC) from contaminated soils in situ, both above and below the water table. The technology is applicable to in situ remediation of contaminated soils well below ground surface, and can be used to treat below or around permanent structures, accelerates contaminant removal rates, and can be effective in all soil types. Steam is forced through the soil by injection wells to thermally enhance the vacuum process. The extraction wells have two purposes: to pump and treat groundwater, and to transport steam and vaporized contaminants under vacuum to the extraction well and then to the surface. Recovered contaminants are either condensed and processed with the contaminated ground water or trapped by gas-phase activated carbon filters. The technology uses readily available components, such as extraction and monitoring wells, manifold piping, vapor and liquid separators, vacuum pumps, and gas emission control equipment.

The SITE demonstration was concluded in April 1992 at a site in Huntington Beach, California. Commercial work at the site by Hughes began in August 1991. The soil at the site was contaminated by a 135,000-gallon diesel fuel spill, and the process appears to have been successful at removing the oil. Quantitative data from the site will be available following an extensive soil sampling and analysis program.

ReTec, Inc., Ukiah, CA. Plasma Arc Vitrification occurs in a plasma centrifugal furnace by a thermal treatment process where heat from a transferred arc plasma creates a molten bath that detoxifies the feed material. Organic contaminants are vaporized and react at temperatures of 2,000 to 2,500°F to form innocuous products. Solids melt and are vitrified in the molten bath at 2,800 to 3,000°F. Metals are retained in this phase. When

cooled, this phase is a nonleachable, glassy residue which meets the TCLP criteria.

Contaminated soils enter the sealed furnace through the bulk feeder. The reactor well rotates during waste processing so that centrifugal forces created by the rotation prevent material from falling out of the bottom and help to evenly transfer heat and electrical energy throughout the molten phase. Periodically, a fraction of the molten slag is tapped, falling into the slag chamber to solidify.

Off-gas travels through a secondary combustion chamber where it remains at 2,000 to 2,500°F for more than 2 seconds. This allows the complete destruction of any organics in the gas. After passing through the secondary combustion chamber, the gases pass through a series of air pollution control devices designed to remove particulates and acid gases.

The SITE demonstration was conducted in July 1991 at a Department of Energy research facility in Butte, Montana. During the demonstration, the furnace processed approximately 4,000 pounds of waste. TCLP testing of the feed and treated soil indicated that only sodium appeared not to be bound in the vitrified slag. No organic constituents were found in the slag, and destruction and removal efficiencies (DREs) for all organics were in excess of 99.99 percent. HCl emissions were very low during the testing program, but $NO_{\rm x}$ emissions were high (approximately 5,000 ppm). It was also observed that the unit requires a high level of maintenance.

SBP Technologies, Inc., Stone Mountain, GA. SBP Technologies, Inc. (SBP), has developed a hazardous waste treatment system consisting of (1) a filtration unit for extraction and concentration of contaminants from groundwater, surface water, or slurries and (2) a bioremediation system for treating concentrated groundwater and soil slurries. These two systems were designed to treat a wide range of waste materials separately or as part of an integrated waste handling process.

The filtration unit is designed to remove and concentrate contaminants by filtering contaminated groundwater through a specially developed membrane. Depending on local requirements and regulations, the filtered product water can be discharged to a publicly owned treatment works (POTW). The concentrated contaminants are collected in a holding tank. The biological system, using a proprietary microorganism mixture, is proposed to biologically destroy concentrated contaminants and produce effluent with low to nondetectable levels of contaminants. Integrating the two units will allow for a variety of contaminants to be removed and destroyed on site.

The first SBP Technologies demonstration, the filtration unit, occurred in September and October 1991 on creosote-contaminated groundwater at the American Creosote Works Superfund site in Pensacola, Florida. During testing, PAH and phenol removal rates of 80 percent were sufficient to pass local POTW discharge standards. Evaluation of the biological treatment system has been postponed.

Toronto Harbor Commissioners, Toronto, Ontario, Canada. The soil recycling project initiated by the Toronto Harbor Commissioners involves a

treatment train of three technologies in series. The treatment is to remove both organic and inorganic materials from the soil and render it reusable. The first technology is a soil washing system to reduce the volume of material handled by concentrating the contaminants in a fine soil slurry. The second technology then removes heavy metals from the concentrated slurry through a process of acid addition and selective chelation. The third technology in the series, chemical hydrolysis and biodegradation, is to destroy the remaining organic contaminants.

Demonstration of the process was accomplished during April 1992 in Toronto, Canada. Approximately 1,050 tons of soil was excavated for the demonstration from the Esso/Texaco site. Contaminants included volatile and semivolatile organics, metals, pesticides, and PCBs. The soil washing portion of the system worked well, however, some operational difficulties were encountered with the other components of the treatment train. Specific results from the demonstration are not yet available.

WASTECH, Inc., Oak Ridge, TN. This solidification and stabilization technology applies proprietary bonding agents to soils, sludge, and liquid wastes with organic and inorganic contaminants to treat the pollutants within the wastes. The waste and reagent mixture is then mixed with cementitious materials, which form a stabilizing matrix. The specific reagents used are selected based on the particular waste to be treated. The resultant material is a nonleaching, high-strength monolith.

The process uses standard engineering and construction equipment. Since the type and dose of reagents depend on waste characteristics, treatability studies and site investigations must be conducted to determine the proper treatment formula. The process begins with excavation of the waste. Materials containing large pieces of debris must be prescreened. The waste is then placed into a high shear mixer along with premeasured quantities of water and SuperSet®, WASTECH's proprietary reagent.

Next, cementitious materials are added to the waste-reagent mixture, stabilizing the waste and completing the treatment process. WASTECH's treatment technology does not generate waste by-products. The process can also be applied $in\ situ$.

A field demonstration at Robins Air Force Base in Macon, Georgia, was completed in August 1991. The WASTECH technology was used to treat high level organic and inorganic wastes at an industrial sludge pit. Preliminary bench-scale results indicate that the organics and inorganics can be immobilized by the technology, but the materials from the field demonstration did not harden as they should. Extremely wet conditions at the site may have influenced the process, but additional applications will be necessary to verify the cementing ability of the technology. Retesting of the system is scheduled for June and July 1992.

Weston Services, Inc., West Chester, PA. The basis of the LT³® technology is the thermal processor, an indirect heat exchanger used to dry and heat contaminated soils. The LT³® process includes three main steps: soil treatment, emissions control, and water treatment. Excavated soil is processed through a shredder to increase the surface area of the soil. (This step may not be needed for sludges or similar matrices.) The conveyor and

surge hopper, which are enclosed to reduce emissions, then feed the soil into the thermal processor. The thermal processor consists of two covered troughs that house four intermeshed screw conveyors. The covered troughs and screws are hollow to allow circulation of hot oil, providing indirect heating of the soils. Each screw moves the soil through the processor and thoroughly mixes the material. Heating of the soil to 400 to 500°F evaporates contaminants, and the vapor stream is then processed through a baghouse dust collector, two condensers in series, and a carbon adsorption unit to remove about 99 percent of the organic contaminants and any particulate emissions. The remaining exhaust gas is continuously monitored to ensure that it contains total organic concentrations not greater than 3 ppm by volume.

Demonstration of the Weston unit took place in November and December 1991 at the Anderson Development Company Superfund site in Adrian, Michigan. The site was contaminated with volatile and semivolatile organics including 4,4'-methylene bis (2-chloroaniline) (MBOCA). The cleanup goal for MBOCA was set at 1.6 ppm by the Michigan Department of Natural Resources. Analytical results from the demonstration are being reviewed.

FUTURE DIRECTION OF SITE

The SITE Program continues to be interested in demonstrations that address source control for soils and sludges, treatment of mixed, low level radioactive waste, *in situ* processes, and combinations of unit operations for total site cleanup. The *in situ* treatment of groundwater, aside from conventional pump and treat systems, is also of high interest to the Agency.

It is anticipated that along with the solicitation of technologies through the Commerce Business Daily, a second major source of demonstration projects over the next several years will be from the SITE Emerging Technology Program. As technologies move through that two-year program, with funding support from EPA, many of them should develop into field-ready processes.

In response to the current interest in innovative technologies by EPA and Federal Agencies such as the Department of Defense and Department of Energy, the SITE Program is also attempting to provide cooperative evaluations of treatability studies and on-going removal or remedial actions. The Program is becoming more flexible in its sampling and reporting efforts so that it can better meet the needs and requirements of these types of sites and clients.

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Potential for Joint Research

Between EPA and the US Army

by

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ABSTRACT

The environmental problems being faced by the US Environmental Protection Agency (EPA) and the US Army are closely related, and the research needed to address them overlaps in many areas. This is especially true in the area of hazardous waste site remediation research aimed at the cleanup of soils, sludges and sediments contaminated by organics and metals. Both EPA and the Army have programs in place to address these needs, and expertise in both agencies can be tapped for site-specific hazardous waste problems.

This paper presents an overview of the hazardous waste site remediation research programs being conducted by EPA's Risk Reduction Engineering Laboratory (RREL) and proposes a number of areas where joint efforts between the two agencies could be mutually beneficial. EPA has established a policy of encouraging the use of innovative technologies that both reduce the quantity of contaminant to be handled and also destroy harmful contaminants. Several technologies, including soil washing, soil vapor extraction, thermal desorption, solvent extraction and soil flushing are of special interest. The RREL has established capabilities for treatability studies and other research endeavors at a number of its locations in Cincinnati, Ohio; Edison, New Jersey; and Jefferson, Arkansas. EPA also continues to foster the use of innovative technologies through its Superfund Innovative Technology Evaluation (SITE) program. In addition, EPA has established a technology transfer program available to other agencies involving both manuals/documents and training personnel. The authors welcome future contacts by Army personnel interested in sharing environmental projects.

INTRODUCTION

The environmental problems being faced by the US Environmental Protection Agency (EPA) and the US Army are closely related, and the research needed to address them overlaps in many areas. This is especially true in the area of hazardous waste site remediation research aimed at the cleanup of soils, sludges and sediments contaminated by organics and metals. Both EPA and the Army have programs in place to address these needs, and expertise in both agencies can be tapped for site-specific hazardous waste problems.

This paper presents an overview of the hazardous waste site remediation research programs being conducted by EPA's Risk Reduction Engineering Laboratory (RREL) and proposes a number of areas where joint efforts between the two agencies could be mutually beneficial. EPA has established a policy of encouraging the use of innovative technologies that both reduce the quantity of contaminant to be handled and also destroy harmful contaminants. Several technologies, including soil washing, soil vapor extraction, thermal desorption, solvent extraction and soil flushing are of special interest. The RREL has established capabilities for treatability studies and other research endeavors at a number of its locations in Cincinnati, Ohio; Edison, New Jersey; and Jefferson, Arkansas. EPA also continues to foster the use of innovative technologies through its Superfund Innovative Technology Evaluation (SITE) program. In addition, EPA has established a technology transfer program available to other agencies involving both manuals/documents and training personnel. The authors welcome future contacts by Army personnel interested in sharing environmental projects.



OVERVIEW OF EPA's RESEARCH PROGRAMS

Approximately 1900 of EPA's 17,000 employees are within the Office of Research and Development (ORD). The research group is divided into eight major offices; ORD operates twelve laboratories throughout the country and has an annual budget of about \$490 million (EPA, 1991a). This is about one third of EPA's operating budget, which excludes major funding programs such as Superfund, the leaking underground storage program and construction grants. The research work directed by EPA is carried out by a combination of federal employees, contractors, and academics. Besides research, ORD also supports technical assistance and demonstrations of new, innovative technologies. Virtually every facet of environmental contamination, including air, water, and solid/hazardous waste, is addressed within EPA's research arena.

In an effort to better focus its research, EPA initiated a new issue-oriented planning process in the fall of 1991. Thirty-nine issues were proposed (Table 1) covering the spectrum of environmental problems. Research strategies and plans for each of these have subsequently been developed. The six-page long research strategies briefly describe the problems and research needs; present EPA's strategic research goals; establish priorities among research needs; focus on the scientific questions that should be addressed; and assign budget allocations to the research priorities. The research plans, varying from 30 to 70 pages each, present more detail on the selection of research areas and on their descriptions, projected products, and budget allocations.

The research plans are important because they define and give priority to what research EPA considers to be important over the next five years. The plan which pertains most directly to hazardous waste sites is "Surface Cleanup". It focuses on the monitoring of

hazardous wastes, quality assurance, development of technologies to clean up hazardous waste sites, and associated technical support. A large part of the Surface Cleanup research plan is on the development and demonstration of innovative technologies that have the potential to reduce the cost of cleanups.

The Surface Cleanup research strategy focuses on four specific areas that should be addressed by EPA's research programs:

- "1. Monitoring. Development of new chemical analytical and bioassessment technologies are needed that are more timely and cost effective in determining both the presence and environmentally safe concentrations of toxic and/or carcinogenic compounds in contaminated sites before, during, and after cleanup operations. Emphasis needs to be placed on real time monitoring techniques that can be used for field screening. Effective representative sampling of contaminated soils and groundwater is also a major problem. This will spur R&D efforts to find alternatives to the use of wells and cores in monitoring the subsurface environment. The emphasis on QA will shift from analytical methods to field sampling QA.
- "2. Technology. The Superfund Innovative Technology Evaluation (SITE) program focus will move toward evaluation of treatment trains and away from single processes and will become even more directly integrated into actual cleanups. Technology will focus increasingly on in-situ technologies to avoid the costs and risks associated with excavation. A major focus will be bioremediation. Emphasis on development of mobile and transportable treatment equipment by EPA will decrease as private sector activities in this area have increased. A substantial new effort will assist the program office in developing standard remedies for classes of Superfund sites.
- "3. Technical Support. The focus increasingly will be on direct site-related cleanup with somewhat less emphasis on development of decisionmaking tools. A monitoring Superfund Technical Assistance Response Team (START) team needs to be created and the technology START team needs to be expanded. Ongoing work on expert systems development will be reoriented toward development of improved engineering decision aids.



TABLE ONE

ISSUE-ORIENTED RESEARCH STRATEGIES AND PLANS

BEING DEVELOPED BY U.S. EPA

A. PROTECTING ECOLOGICAL SYSTEMS

Ecosystems

- 1. Coastal and marine
- 2. Large lakes and rivers
- 3. Wetlands
- 4. Terrestrial systems

Assessments

- 5. Contaminated sediments
- 6. Aquatic ecocriteria
- 7. Nonpoint sources
- 8. Ecorisk assessment methods

Emerging Ecological Issues

- 9. Habitat/biodiversity
- 10. Environmental releases of biotechnology products

B. ENVIRONMENTAL MONITORING AND ASSESSMENT

11. EMAP

C. GLOBAL CHANGE

- 12. Global warming
- 13. Stratospheric ozone depletion

D. AIR POLLUTION

- 14. Acid deposition/aerosols
- 15. Air toxics
- 16. Criteria air pollutants
- 17. Pollutants from motor vehicles
- 18. Indoor air pollution

E. DRINKING WATER CONTAMINATION

- 19. Drinking water pollutants and disinfection
- 20. Ground water

F. FOOD SAFETY

21. Toxics in food

TABLE ONE (continued)

ISSUE-ORIENTED RESEARCH STRATEGIES AND PLANS BEING DEVELOPED BY U.S. EPA

G. WASTE MANAGEMENT

- 22. Municipal solid waste
- 23. Hazardous waste
- 24. Sludge and wastewater

H. ENVIRONMENTAL CLEAN-UP

- 25. Surface cleanup
- 26. Bioremediation
- 27. Spills to surface water

I. IMPROVING HUMAN HEALTH RISK ASSESSMENT

- 28. Human exposure
- 29. Health effects
- 30. Risk assessment methods

J. INNOVATIVE TECHNOLOGY AND OUTREACH

- 31. Pollution prevention
- 32. Innovative technologies
- 33. Environmental education
- 34.International and national technology transfer

K. EXPLORATORY RESEARCH AND SPECIAL

ENVIRONMENTAL PROBLEMS

- 35. Environmental review of new chemicals
- 36. Multi-media nitrogen impacts
- 37. Lead and other heavy metals
- 38. Anticipatory research on emerging environmental problems
- 39. Exploratory grants and centers

L. INFRASTRUCTURE



"4. University Research Centers. The Superfund law mandates the establishment of five university-based, regional hazardous material research centers. Additionally, Congress provides funding for the Clark Atlanta and Gulf Coast (Lamar University) Hazardous Waste Research Centers. EPA is attempting to more closely integrate the activities of these centers with the rest of the Superfund R&D program. (Source: EPA, 1992a)

The remainder of this paper will focus on the technology and technical support areas.

The technology area of the Surface Cleanup research plan addresses the SITE program; new research directions in the separation and extraction of contaminants from soil, sludges, and sediments; evaluations of material handling techniques; incineration research; in-situ treatment research; and the development of standard remedies. Each of these areas is described more fully below.

OVERVIEW OF THE RISK REDUCTION ENGINEERING LABORATORY

The Risk Reduction Engineering Laboratory (RREL) is EPA's largest laboratory; its mission centers on engineering research aimed toward the "prevention, control, and treatment of hazardous and nonhazardous wastes, including those at Superfund sites. These investigations include defining and characterizing sources of pollution, and developing advances in the state of the art of pollution control. RREL also provides engineering concepts for cost-effective engineering solutions to difficult pollution problems, and for anticipating and recommending solutions to emerging environmental problems." (EPA, 1992b)

Organizationally, RREL includes approximately 200 scientists and engineers divided among four divisions. The Superfund Technology Demonstration Division is primarily responsible for the Superfund Innovative Technology Evaluation (SITE) program; provision of technical support to EPA regional offices; research and development of technologies to

treat contaminated soils; research for prevention, leak detection and corrective actions for contamination from underground storage tanks (USTs); research supporting cleanup of spills of oil and hazardous chemicals; and evaluation of protective clothing and personnel protection systems.

RREL Research Facilities

RREL's main offices are located in Cincinnati, Ohio. RREL also operates four major satellite facilities:

- Edison, New Jersey the RREL units located here are responsible primarily for soils contamination research, Superfund/hazardous waste site treatability studies, the UST research program, the oil/chemical spills research program, the personnel protection research program, technical assistance to regional remedial project managers (RPMs), and the stormwater/combined sewer research program;
- Test and Evaluation (T&E) Facility, Cincinnati, Ohio the T&E
 Facility is predominantly concerned with studies in the areas of
 municipal/industrial wastewater and hazardous waste treatment;
- Center Hill Research Facility, Cincinnati, Ohio the major activities here focus on chemical solidification and stabilization; treatability studies; in-situ physical, chemical, and biological treatment of contamination soils; and utilization and disposal of hazardous and municipal solid wastes;
- Incineration Research Facility (IRF), Jefferson, Arkansas two pilotscale incinerators (a rotary kiln and a liquid injection system) located here support studies in hazardous waste incineration.

RREL also operates other facilities, including the Full Containment Facility, Drinking Water Pilot Plant, Mobile Wastewater Treatment Units, Mobile Dehalogenation Treatment Units, a Mobile Volume Reduction/Soils Washing Unit, the Synthetic Soils Matrix (SSM) Blending Facility, and the Underground Storage Tank Test Apparatus (EPA, 1989a). Table 2 gives points of contact for these research facilities.



Past Accomplishments

A review of the major accomplishments of the entire RREL is beyond the scope of this paper. However, some highlights from the research conducted at RREL's Edison, New Jersey facility (EPA, 1990) are given below.

The research milestones of the Edison ORD facility lie in six directions:

- evaluating and improving new hazardous waste (Superfund) treatment technologies;
- detecting/cleaning up leaks from USTs;
- cleaning up oil spills that threaten our waterways;
- preventing pollution from contaminated stormwaters;
- improving protective equipment for environmental personnel;
- controlling hazards that result from chemical spills.

A number of innovative technologies were developed and demonstrated in Edison: the EPA mobile incineration system (MIS), which was eventually used to clean up dioxin-contaminated Superfund sites throughout southern Missouri and served as a model for mobile incinerators in common use today; a mobile soils washing system, which is used to separate the highly contaminated particles from a soil, thereby reducing the volume requiring further treatment/disposal (this has also been replicated commercially); the mobile physical-chemical treatment system, which was used in the 1970's to enhance treatment at chemical spills sites and hazardous waste sites (also commercialized); a mobile carbon regeneration system, which could be used to renew spent granular activated carbon for reuse; and a mobile laboratory, which could be taken on-site for rapid analytical support (also commercialized).

TABLE TWO EPA CONTACTS IN KEY RESEARCH AREAS

Research Area/Facility	EPA Contact	Telephone Number
OVERALL FACILITATOR	Daniel Sullivan	(908) 321-6677
RREL - Edison, NJ Facility	Daniel Sullivan Jack Farlow Frank Freestone	(908) 321-6677 (908) 321-6635 (908) 321-6632
RREL - Cincinnati Test and Evaluation (T&E) Facility	Frank Evans	(513) 684-2621
RREL - Center Hill Facility	Bob Landreth	(513) 569-7871
RREL - Incineration Research Facility	Clyde Dempsey	(513) 569-7504
SITE Program - Demonstrations - Emerging Technologies	John Martin Norma Lewis	(513) 569-7758 (513) 569-7665
Technology Development - separation and extractions - materials handling	Rich Griffiths Mike Borst Clyde Dempsey Mike Roulier Carlton Wiles Bob Landreth Daniel Sullivan Ben Blaney Frank Freestone Ed Bates	(908) 321-6629 (908) 321-6631 (513) 569-7504 (513) 569-7796 (513) 569-7795 (513) 569-7871 (908) 321-6677 (513) 569-7406 (908) 321-6632 (513) 569-7774
Technology Transfer	Joan Colson	(513) 569-7501
Treatability Studies	Rich Griffiths Gene Harris	(908) 321-6629 (513) 569-7862



TABLE TWO (continued)

EPA CONTACTS IN KEY RESEACH AREAS

Technical Assistance		
- site specific	Frank Freestone	(908) 321-6632
	Ed Bates	(513) 569-7774
 waste minimization/pollution prevention 	Jim Bridges	(513) 569-7683
Federal Technology Transfer Act		
Cooperative Agreements		
- mobile incinerator system	Daniel Sullivan	(908) 321-6677
 in-situ containment treatment unit 	Mike Borst	(908) 321-6631
- mobile soil washer	Hugh Masters	(908) 321-6678

SITE Program

The Superfund Amendments and Reauthorization Act of 1986 (SARA) required EPA to establish an "Alternative or Innovative Treatment Technology Research and Demonstration Program" for testing innovative treatment technologies at Superfund sites. EPA's SITE program was established in response to that requirement.

EPA encourages the use of innovative technologies for the treatment of hazardous wastes: solutions need to be more effective, permanent, and cheaper. Landfill space is becoming limited, while the hazardous waste problem is substantial and likely to be with us for several decades. One of the major goals of the SITE program is to provide objective, independent data on new remediation technologies in order to provide regional project managers with a sound basis for selecting permanent, innovative/alternative solutions that are protective of human health and the environment.

The SITE program has four components: Demonstration Program, Emerging

Technologies Program, Monitoring and Measurement Technologies Program, and the

Technology Information Services. In the Demonstration Program, innovative technologies

are tested and evaluated by EPA in accordance with the Agency's quality assurance

principles, and that data is made available to the public through a series of evaluation

reports. Eighty-one projects are currently in the demonstration program. In the Emerging

Technologies Program, new technologies which have been successfully proven at the bench

scale are brought to the pilot scale level and then tested independently by EPA. About forty

emerging technologies are currently in this program.



Cooperative Research with the Air Force

There are a number of projects in the Emerging Technologies Program which are jointly funded by EPA and the U.S. Air Force. These projects address innovative technologies which have potential to be used to address problems at Department of Defense (DOD) installations. The resources provided by the Air Force for these evaluations includes funds but also collaborative efforts by Air Force personnel.

ONGOING RREL RESEARCH IN THE HAZARDOUS WASTE AREA

Every year, the RREL hosts a research symposium to make the results of recently-completed projects available to the user community and to report on the progress of projects currently underway. Over 45 technical presentations and 30 poster displays were presented at the 1992 three-day conference. Proceedings from these conferences are available (EPA, 1992c).

Some highlights of on-going research in the hazardous waste area are given below.

These have been extracted from the EPA Surface Cleanup Research Plan.

Separation and Extraction Technologies

These physical and chemical processes are used to remove contaminants from soil without destroying the contaminants (or the soil). They are typically applied to excavated soils. The current program has three components:

- several basic research efforts address the physical and chemical interactions of soil and contaminants in order to learn better how to separate the two;
- several bench-scale experimental efforts evaluate the potential of new processes;

pilot-scale experiments generate more complete engineering data on the more promising technologies, including the work on the Volume Reduction Unit (a pilot-scale soils washing system).

The three components are designed to be complementary.

Materials Handling Technologies

All treatment methods that involve soil excavation require material handling prior to treatment. Dusts and vapors generated during excavation, soil screening, debris separation, and soil blending operations can contain contaminants. Current research would look at methods to control dust and vapors, supported by field observations and surveys. Ongoing work in this area, however, is minimal.

Incineration Research

While hazardous waste incineration is a proven technology which is the most effective and widely applicable control technology available today for the treatment of a wide range of organic hazardous waste, its effective implementation at specific Superfund sites has been greatly impeded. Considering that incineration is the chosen remediation technology for approximately two hundred Superfund projects, substantial delays are likely to occur if these impediments are not removed. The issues that need to be addressed include:

- control of heavy metals emissions metal emissions have been the
 dominant component of the risk associated with incineration operations,
 and more work on the fate (or "partitioning") of metals in the
 combustion process and the effectiveness of air pollution control
 devices (APCDs) to control metals emissions;
- evaluation of novel incineration operating modes and systems in order to address unique Superfund wastes;
- evaluation of untested/unique Superfund wastes;



- examination of existing real-time monitoring systems and approaches to reliably predict/detect process failure; and
- evaluation of organic combustion byproducts to better define whether or not a problem exists due to the emission of organics.

A risk assessment/incineration primer is also being developed by EPA to be used at public meetings to address the concerns raised.

Another area of incineration research is being done through a Federal Technology

Transfer Act (FTTA) cooperative agreement in the form of demonstrations of incineration

capability using the mobile incinerator system (MIS) developed by RREL. EPA's industrial

partner, Vulcan Iron Works, is in the process of revamping the mobile incinerator and will

make it available for on-site demonstrations of incineration technology.

In-Situ Treatment

One of the major advantages of in-situ treatment is that it avoids the risk of discharging contaminated particulates or volatile organics because the soil isn't moved.

RREL has identified four areas needing further work:

- delivery/recovery systems methods of moving treatment materials into the soil and removing residuals and excess materials after treatment hydrofracturing and pneumatic fracturing are promising methods;
- mixing systems improvements in the efficiency of mixing would contribute to the success of in-situ treatment - development of methods to measure the uniformity of mixing in-situ is the most urgent need;
- controlling movement the lack of methods to control movement of treatment chemicals in unsaturated soils will severely limit the application of in-situ chemical treatment - electrokinetics and freezing have potential for creating temporary near-surface perched water tables to control movement of treatment fluids; and

 controlling critical conditions - the performance of in-situ treatment processes is affected by physical and chemical conditions (e.g. pH, redox, temperature) in the soil - the critical conditions need to be identified and methods developed for controlling them in-situ so that treatment processes can be optimized.

Much of this work is being done in cooperation with the University of Cincinnati at the RREL Center Hill Facility. The major activity is in delivery/recovery systems.

Standard Remedies Development

A new initiative will begin in FY93 to develop standard remedial technologies for sites that are not unique, including lead battery, wood preservative, and town gas sites. This should reduce the time and cost to identify remedies for these categories of Superfund sites, which have already been characterized and much is known about the contaminant present, soil conditions, site locations, and target treatment goals. Since these sites are similar, a standard treatment system should be applicable.

Waste Minimization/Pollution Prevention Programs

Pollution prevention is a cornerstone of EPA programs to reduce the adverse impacts associated with environmental contamination. A major effort conducted by RREL is the Waste Reduction Evaluations at Federal Sites (WREAFS) program, wherein EPA works with other federal agencies to assess waste minimization opportunities, demonstrate pollution prevention techniques, and conduct workshops. A number of joint evaluations have with the Departments of Agriculture, Defense, Energy, Interior, Transportation, Treasury, and Veteran Affairs; the results of each study have wide application to similar situation in many other agencies.

While the waste minimization assessments are an important part of this program, the current focus is to move forward to joint R&D efforts to enhance pollution prevention

benefits in the federal community. EPA is currently working with DOD counterparts and others to determine R&D needs.

TECHNICAL SUPPORT AND EPA TECHNOLOGY TRANSFER PROGRAMS Technical Support

A good portion of RREL's work is providing technical assistance to RPMs addressing Superfund and Resource Conservation and Recovery Act (RCRA) hazardous waste sites. There are two components: site-specific assistance and technology transfer. The principal site-specific assistance is provided through the Superfund Technical Assistance Response Team (START), a group of research engineers and scientists who review site data and advise regional clientele on appropriate treatment technologies. There is both short-term handling of day-to-day requests and long-term support on more complex Superfund sites. This program also sponsors a publically-available on-line data base for treatment technology information, as discussed below.

Technology Transfer Program

A major component of EPA's research program in the hazardous waste area is technology transfer, implemented through a series of publications and training workshops. In FY92, EPA completed three treatability assistance guides, thirteen engineering bulletins and two site-category treatment technology resource documents. Further, through its Superfund University Training Institute, EPA offers several training courses on hazardous waste treatment, emphasizing innovative technologies. Finally, EPA has established a number of databases to centralize data concerning hazardous waste cleanup operations: these include the Alternative Treatment Technology Information Center (ATTIC) database, the Computerized On-Line Information System (COLIS), and a treatability study database.

MECHANISMS FOR JOINT RESEARCH

The major mechanism for joint research between EPA and other federal agencies is through the use of an interagency agreement. In a less formal sense, however, periodic communication between principal researchers, joint publications, and other collaborative efforts are all valid means to exchange information, data and ideas.

EPA links research efforts with academia and private industry through a number of grants and cooperative agreements. Under the Federal Technology Transfer Act (FTTA), EPA has signed agreements with numerous industrial partners to promulgate research products through demonstrations. Many of the technologies already developed could be applied to hazardous waste problems at U.S. Army facilities.

KEY AREAS OF EPA INTEREST

The areas where EPA would be most interested in cooperative research with the US Army are summarized in Table 3 and discussed below. The contaminants most commonly faced include trichloroethylene (TCE) and other solvents; lead and other heavy metals; and polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and other semi volatiles.

Demonstration of Volume Reduction Technology

RREL has recently completed design and fabrication of a mobile (100 lb per hour - pilot scale) volume reduction unit (VRU) for soil washing. This unit is currently being used but will be available for demonstrations of volume reduction at hazardous waste sites.

In most cases, soil washing technologies are used in conjunction with other remedial methods for the separation/segregation and volume reduction of hazardous materials. The



actual process consists of several steps: mixing of feed water and various extraction agents to remove the contaminants from soil, sorting out the soil particles by size, and cleaning of the large soil fraction for safe return to the site. The smaller contaminant fraction, suspended in the washing fluid, is then recovered as sludge, either by flocculation with a selected polymer or other chemical, followed by settling, or by gravity alone (EPA, 1991b).

Performance of Treatability Studies

Treatability studies are an important component of both the remedial investigation/feasibility study (RI/FS) planning process and the remedial design/remedial action (RD/RA) design/construction process under SARA. It is essential to conduct laboratory and/or pilot-scale tests on actual wastes from the hazardous waste site. The management review conducted in 1989 of EPA's Superfund program concluded that:

"These 'treatability tests' are not currently being performed at many sites to the necessary extent, or their quality is not adequate to support reliable decisions." (EPA, 1989b)

RREL has defined four levels of treatability studies:

- literature review this compares what is already known about technologies with the site characterization data;
- remedy screening study this is a small scale (jar test) evaluation done
 in the laboratory it provides approximate qualitative results the cost
 for this study is about \$20,000 \$50,000 for each technology
 evaluated;
- remedy selection study this is usually done to confirm whether a
 proposed remedy is valid for that particular site and to generate more
 quantitative data for estimating cost and performance it is needed to
 complete the ROD its cost is usually from \$50K to \$250K;

TABLE THREE AREAS OF EPA INTEREST FOR JOINT EPA-ARMY RESEARCH EFFORTS

Demonstration of the Volume Reduction Unit Performance of Treatability Studies

- literature review
- remedy screening study
- remedy selection study
- pilot scale testing
- incineration of untested and unique Superfund wastes
- soil washing
- soil vapor extraction
- thermal desorption
- solvent extraction
- soil flushing

SITE Demonstrations at Federal Facilities

Technical Assistance in Treatment Technology Areas

- soil washing
- soil vapor extraction
- thermal desorption
- solvent extraction
- soil flushing

pilot-scale testing - this is large scale (room size equipment), usually done after the ROD is published to confirm engineering design parameters - its cost runs in the \$250K to \$1,000K range.

RREL has developed capability to conduct these treatability studies at all of its satellite facilities. Table 2 gives a summary of the capabilities within each of the major study areas.

Six areas where treatability study support could be given by EPA include incineration of untested/unique Superfund wastes, soil washing, soil vapor extraction, thermal desorption, solvent extraction, and soil flushing.

SITE Demonstrations at Federal Facilities

In 1986, when the SITE program was established, most technology demonstrations were selected through an annual solicitation to the public and industry. This process, still conducted, has yielded over 80 SITE demonstration projects. In addition to the annual solicitation, projects can be entered into the demonstration program from the emerging technology SITE program or directly upon the recommendation of a hazardous waste site Remedial Project Manager (RPM).

EPA encourages testing of innovative technologies at hazardous waste sites and is interested in joining that effort with SITE demonstration funds. If a remedy selected for a site is innovative (currently, almost all technologies other than established versions of incineration and solidification/stabilization are "innovative"), EPA will readily participate with funds to evaluate that technology.

Technical Assistance in Treatment Technology Areas

The RREL has been providing technical assistance to EPA regional offices through its START program for the past several years. The treatment technology areas and points of

contact at RREL are given in Table 2. These personnel may be contacted to discuss joint research projects. Areas of particular EPA interest include soil washing, soil vapor extraction, thermal desorption, and solvent extraction.

CONCLUSIONS

There are a number of common problems that EPA and the U.S. Army face in cleaning up hazardous waste sites. Communication between the two agencies is imperative; coordination on common research areas is warranted. This paper summarizes several approaches being taken by EPA to address the problems at hazardous waste sites and presents a few key areas where joint research between the two agencies would be beneficial; EPA contacts are given so that follow up activities can occur.

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INTEGRATION OF PHYSICAL AND BIOLOGICAL TECHNOLOGIES FOR SITE REMEDIATION: A CASE HISTORY

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ABSTRACT

Effective remediation of sites containing mixtures of organic chemicals in soil and groundwater often require the combination of various treatment technologies. For this project, an onsite treatment system was designed and implemented to remediate soil contaminated with fuel hydrocarbons and groundwater containing several volatile organic compounds such as 1,1,1-trichloroethene, methyl ethyl ketone, and benzene. This case history describes:

- Site characterization
- Laboratory evaluation of biological treatment
- Field results indicating removal of the contaminants in soil and groundwater

The onsite integrated treatment system results in a viable, cost-effective solution to a complex environmental problem.

BACKGROUND

Historical Background

Established in 1962, the Fire Drill Area (FDA) is a former training site used by the Fort Ord Fire Department. Training sessions were conducted one weekend a month, and four to five burns were initiated on Saturday and again on Sunday. During each practice burn, the ground surface was first watered down. The fuel storage tank valve was opened and the burn pit flooded with approximately 150 to 200 gallons of fuel and other flammable materials, which were subsequently ignited. Although the practice fires were extinguished primarily with water, nontoxic chemical foam was used occasionally, but not often due to its high cost. Firefighting training activities at the FDA were suspended in 1985.

Approximately 90 percent of the fuel burned at the FDA was reported to be JP-4 helicopter fuel that was either water-contaminated or outdated. Other substances burned at the site included hydraulic and lube oils, gasoline, diesel fuel, and small quantities of industrial solvents. Most of the fuels were collected at airfield hangars by military personnel. The waste products were brought to the site primarily in drums and then transferred into the fuel tank or stored; however, the drums were occasionally dumped down the hillside or emptied directly onto the burn pit. Surplus 600-gallon water tank trailers were also used to store excess and spent fuels. Apparently, one or more of these trailers may have been hauled to the site and allowed to empty onto the ground. Because of the potential for soil and groundwater contamination, the

California Regional Water Quality Control Board (RWQCB) requested the Army to investigate and, if warranted, remediate the FDA site.

Site Description

The FDA is located near the northern boundary of Fort Ord, just west of Fritzsche Army Airfield, near Monterey, California. Fort Ord is bounded by Monterey Bay to the west and by State Highway 68 and bedrock highlands of the Santa Lucia Range to the south. The FDA lies within a topographic depression of wind-blown dune sand deposits; this depression appears to have been graded somewhat to facilitate its use as a firefighting training facility. The surrounding terrain comprises gently rolling hills consisting of dune sands vegetated with mature grasses, shrubs, and trees.

The Site Plan, Figure 1, illustrates the FDA vicinity. The burn pit is a nearly level area approximately 140 feet in diameter that is surrounded by a shallow containment ditch. The surface of the burn pit has been blackened by firefighting training activities and contained burned cars and truck bodies. On the north side of the FDA, a dirt road extends from the locked entrance gate to a former drum storage and fuel unloading area. Surface soil in the vicinity of the drum storage and unloading area are stained black from spilled material. Downslope of this area is an aboveground fuel storage tank. Fuels were gravity-fed from the tank to a spray nozzle in the center of the burn pit.

Climate and Topography

Fort Ord is located in a coastal area that has a Mediterranean climate characterized by mild summers, with temperatures ranging between 54° and 80°F, and mild winters, with temperatures ranging between 35° and 65°F. Rainfall in 1985 at Fritzsche Army Airfield was 14.7 inches, 90 percent of which occurred from January through May, and October through December. Normal annual rainfall at Fort Ord is about 14 inches.

The burn pit lies within a topographic depression of dune sand deposits ranging in elevation from 124 to 125 feet above mean sea level (MSL). The surface of the central portion appears to have been graded somewhat to facilitate its use as a firefighting training area. Because of the high permeability of the sandy soil in the area, rainfall percolates directly into the soil. Runoff rarely occurs at the FDA because it is essentially undeveloped, and no pavement or facilities exist at the site.

Hydrogeology of the Fort Ord Area

Based on available literature and information derived from this study, the general hydrogeologic environment in the vicinity of Fort Ord includes a system of unconfined and semi-confined aquifers that extend offshore beneath Monterey Bay. This system is characterized by at least two, and perhaps three, clay layers that divide the system into four aquifer zones known as the uppermost, 180-foot, 400-foot, 900-foot aquifers (Figure 2). The uppermost aquifer is comprised of dune sands and is typically present in the vicinity of the FDA at depths ranging from 60 to 80 feet. The unit is unconfined and approximately 20 to 30 feet thick. The uppermost aquifer is separated from the next major aquifer by a thick clay unit known locally as the Salinas Valley Aquiclude. This layer is approximately 50 to 100 feet thick and is composed predominantly of silt and clay with some interbedded but discontinuous The 180-foot aquifer is typically present at depths of approximately 200 to 250 feet below ground surface and consist of approximately 50 to 150 feet of interbedded sands and gravels. The 180-foot aquifer is confined by the Salinas Valley Aquiclude and underlain by the 400-foot aquifer. This unit is a hydraulic connection with the 180-foot aquifer in the Fort Ord vicinity but confined elsewhere. A clay unit separates the 400-foot aquifer from the

900-foot aquifer. The deeper aquifers, 180-foot, 400-foot, and 900-foot, are all used for water supply in the Fort Ord and Salinas Valley. Because of the thick clay unit separating the uppermost aquifer from the deeper zones, the uppermost aquifer was targeted for this investigation.

Generally, the uppermost aquifer is poorly documented, however, it is known, that this aquifer has been used historically as a source for domestic water supply, and that the regulatory agencies have identified present beneficial uses of this source to include domestic, agricultural, and industrial water supplies. Consequently, HLA initiated a site investigation program to evaluate the presence of chemicals in soil and groundwater underlying the FDA.

SITE CHARACTERIZATION

Summary of Groundwater Contamination

Ten monitoring wells, installed in the uppermost aquifer, were monitored and sampled quarterly for two years to provide hydrogeologic and water chemistry data. Petroleum hydrocarbons, organohalides, aromatic hydrocarbons, methyl ethyl ketone (MEK), and metals were detected in the groundwater during the groundwater investigation. Petroleum hydrocarbons were detected at concentrations below 1 milligram per liter (mg/l) in groundwater samples from the uppermost aquifer. Trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and trans-1,2-dichloroethylene (DCE) were the principle organohalides detected in maximum concentrations of 650 micrograms per liter (μ g/l), 1.3 μ g/l, and 49 μ g/l, respectively. Aromatic hydrocarbons, benzene, toluene, xylenes, and ethylbenzene were also detected. MEK was found in groundwater samples at concentrations ranging from 120 to 3,200 μ g/l. Priority pollutant metal analyses detected low levels of chromium, zinc, and mercury in the groundwater. Only TCE and MEK concentrations were detected at levels exceeding state or federal action levels.

Summary of Soil Contamination

In general, results of the site characterization indicated that light and heavy total petroleum hydrocarbon (TPH) are present in near-surface soil (0 to 15 feet in depth) and the vadose zone (greater than 15 feet in depth) at the burn pit. Light and heavy TPH was detected in near-surface soil at concentrations ranging from less than 0.5 to 16,000 milligrams per kilogram (mg/kg). Concentrations in the vadose zone were generally less than 10 mg/kg. Toluene and xylenes were detected in a few of the surface soil samples (less than 5 feet in depth) collected near the center of the burn pit, the drum storage area, and at the entrance gate to the FDA. These concentrations ranged from 2 to 51 micrograms per kilogram (μ g/kg), 4 to 20 μ g/kg, and 2 to 24 μ g/kg, respectively. Benzene was also detected in two surface samples collected from the drum storage area at concentrations ranging from 3 to 5 μ g/kg. In addition, at one surface sample location (1 to 2.5 feet in depth) near the center of the burn pit, the following chemicals were detected at the concentrations noted: ethylbenzene, 2 to 27 μ g/kg; benzene, 3 to 12 μ g/kg; MEK, 600 to 2,900 μ g/kg; TCE, 47 μ g/kg; and TCA, 76 μ g/kg.

The results of the soil investigation indicate three primary areas where chemicals were detected. Elevated levels of TPH, toluene, and xylenes were detected near the center of the burn pit, the drum storage area, and at the entrance gate to the FDA. High concentrations of TPH, ethylbenzene, benzene, MEK, TCE, and TCA were also detected near the center of the burn pit. The areas in the immediate vicinity of the burn pit and at the entrance gate to the FDA where the above chemicals were detected in soil correlate closely with the locations where elevated levels of similar chemicals, including benzene, toluene, xylenes, ethylbenzene, and DCE, were detected in a soil gas study conducted prior to installation of wells and soil borings.

Biological Assessment

To assess the potential for using a biological remediation technique, inorganic nutrient and microbial enumeration evaluations of soil samples were conducted. The microbiological evaluation indicated that an indigenous population of hydrocarbon utilizing microorganism existed in the hydrocarbon-bearing soil. Results of the inorganic nutrient evaluations indicated that nitrogen as ammonia or nitrate and phosphorus as orthophosphate were present in concentrations that could potentially limit microbial metabolism. The addition of a prepared nutrient formulation to the site soil in a laboratory study results in the stimulation of the hydrocarbon utilizing microbial population. The results of the laboratory study indicated that bioremediation was technically feasible for treatment of the hydrocarbon-bearing soil.

REMEDIAL ACTION PROGRAM

The remedial action program developed for groundwater was to operate two extraction wells to 1) prevent the downgradient migration of contaminated groundwater away from the FDA, 2) diminish vertical groundwater migration, and 3) remove groundwater from areas of the uppermost aquifer in which chemicals have been detected. Extracted groundwater would be treated by aqueous activated carbon adsorption to remove volatile organic compounds (VOCs).

The remedial action program developed for soil was excavation with enhanced soil biodegradation. The soil treatment system includes two areas: a biotreatment area and an excess spray area. Hydrocarbon-contaminated soil in the biotreatment area are sprayed with nutrient-enriched effluent from the groundwater treatment system. The nutrients accelerate the biological degradation of the hydrocarbons in the soil. This remedial alternative was also compatible with the recommended groundwater remediation program.

The remediation system involved groundwater extraction, treatment by activated carbon adsorption to remove VOCs, and enhancement of soil microbial action to provide biodegradation of MEK in the effluent (activated carbon is not effective in its removal) and hydrocarbon in the soil (Figure 3). Because the soil treatment and groundwater treatment remedial actions use similar technologies and share the same treatment site, the most cost-effective method of accomplishing the goals of these separate remedial efforts was to integrate them.

The groundwater treatment portion of the project involved implementing the following steps:

- Groundwater was extracted from a system of recovery wells. Two piezometers were installed near each extraction well as part of the monitoring program to evaluate the effectiveness of the groundwater treatment system.
- The groundwater was pH-adjusted and then passed through an activated carbon adsorption unit to remove volatile organic compounds. The groundwater and soil treatment system process equipment was installed between March 23 and April 9, 1988. Activities included construction of the equipment and transformer pads, installation of extraction well pumps, discharge and nutrient metering pump, carbon canisters, and related plumbing, meters, gauges, electrical systems, and control panels. This equipment was installed following HLA design specifications except that a third sprinkler was added to the effluent discharge system to provide additional coverage to the expanded biotreatment area.

The effluent was supplemented with nutrients, and applied to the excavated and tilled soil via fine mist spray nozzles. Effluent not used for biological treatment was sprayed in a recharge area upgradient of the treatment system.

The soil remediation portion of the project involved implementing the following steps:

- Excavation of soil from the burn pit and temporary stockpiling of approximately 4,000 cubic yards of soil containing hydrocarbon at levels above RWQCB guidelines.
- Subsequent backfilling of the excavation with clean soil (i.e., soil having concentrations below RWQCB guidelines).
- Distribution of stockpiled hydrocarbon-containing soil to a uniform depth in the biotreatment area for bioremediation. The biotreatment area is approximately centered in the area of the old burn pit.
- After the contaminated soil was distributed in the biotreatment area, six pressure vacuum lysimeters were installed in the biotreatment and excess spray areas to monitor for leachate migration from the biotreatment area into the underlying soil.
- Nutrients necessary to enhance biodegradation of both the soil and groundwater contaminants were added to the groundwater treatment system effluent. Enhanced biodegradation will commence when effluent from the groundwater treatment system is applied to the tilled soil.
- The treated soil were tilled on a periodic basis to enhance biological treatment.

TREATMENT SYSTEM OPERATION

Operation of System

Groundwater remediation involved extraction and carbon treatment of the contaminated groundwater. Water was extracted from downgradient Extraction Wells FX-01-A and FX-02-A (Figure 4). The extracted groundwater is pumped directly through two granular activated carbon (GAC) canisters in series to remove VOCs and hydrocarbons. This treatment process removes the organic contaminants previously identified in groundwater at the FDA except for a portion of the MEK. Most of the MEK, if present, in the extracted groundwater is adsorbed by the GAC; MEK remaining in the effluent either volatilizes in the spraying process (see below) or is biodegraded in the soil treatment process.

The soil treatment system includes two areas: a biotreatment area and an excess spray area (Figure 5). Hydrocarbon-contaminated soil in the biotreatment area are sprayed with nutrient-enriched effluent from the groundwater treatment system. The nutrients accelerate the natural biological degradation of the hydrocarbons in the soil. Soil moisture is maintained at an optimum level of 5 to 15 percent by weight to promote microbial growth. The moisture level is maintained by spraying the effluent at a predetermined rate over the area using an automatic timer and valve system. Effluent not sprayed in the biotreatment area is released in the excess spray area upgradient of the biotreatment area.

First Operational Period - August 1988 through May 1989

On July 27, 1988, performance tests of the treatment system were conducted by HLA. Extraction well flow rates were balanced, the fertilizer metering pump was adjusted, and the system's protection features were checked. In addition, sprinkler operation intervals in the biotreatment and excess spray areas were adjusted to provide the proper amount of effluent to each area. Later the same day, after completion of the performance test, the groundwater and soil treatment system was placed on continuous automatic operation.

The treatment system operated continuously from late July 1988 to May 1989 except for minor shutdowns for routine maintenance.

Breakthrough of VOCs from the carbon canisters at the treatment system was first observed in February 1989 and continued into May 1989. In early May 1989, the maximum effluent contaminant concentration level defined by the RWQCB was exceeded and the treatment system was subsequently shutdown on May 19, 1989. Approximately 4,380,000 gallons of extracted groundwater had been treated prior to the shutdown.

Design Modifications

During the system shutdown from May through November 1989, design modifications were completed to increase the efficiency of the system.

The original design specifications and subsequent construction of the groundwater treatment system allowed for a maximum influent flow rate of approximately 15 gallons per minute (gpm) or less at a maximum pressure of 12 pounds per square inch (psi). However, monthly monitoring results indicated that extraction well capacity exceeded the system design criteria, which were based on aquifer testing. It appeared that several feet of available drawdown present at both wells could be utilized by increasing the efficiency of the extraction system.

To increase the efficiency of the groundwater extraction and treatment system, larger piping, larger capacity GAC canisters and appropriate replacement process controls were installed to allow for a maximum influent rate of approximately 20 gpm.

Current Operation Through May 1991

As mentioned in First Operational Period Section, the groundwater treatment system was shut down on May 19, 1989, after contaminant concentrations in the system effluent exceeded the maximum allowable levels. In addition to the previously mentioned design modifications, in November 1989, the upper 12 inches (first lift) of treated soil in the biotreatment area was removed.

From June through October 1989, collection and chemical analysis of water and soil samples were discontinued, as was collection of soil samples for microbial and soil moisture analysis. Measurement of monitoring well water levels continued on a reduced schedule. In early November 1989, soil and water sample collection and analysis were reinstated prior to treatment system startup. The treatment system was restarted on November 27, 1989.

The groundwater treatment system has operated continuously since the second startup on November 27, 1989, except for short-term shutdowns for minor repairs or routine maintenance. Minor interruptions to the operation of the soil treatment system are discussed below.



Chemical Mass Removal

Groundwater

The estimated mass of volatile organic chemicals extracted and treated by the groundwater treatment system has been determined quarterly since the system began operation in August 1988. For each quarter, this estimate was calculate by multiplying the volume of groundwater treated each month by the difference between the concentration of each major compound detected (1,1,1-TCA, total 1,2-DCE, 1,1-DCA, 1,1-DCE, TCE, PCE, and chloroform) in the monthly samples from the combined influent sampling port and the concentrations detected in samples from the effluent port. The masses of the individual compounds removed were then summed to estimate the total chemical mass removed for that month; these monthly values were then summed to provide an estimate of the total chemical mass removed for the quarter (Figure 6).

The total chemical mass removed during operation of the treatment system from August 1988 through May 1991 was approximately 17 pounds. Of this total, approximately 10 pounds of contaminants were removed from the groundwater during the first operational period from August 1988 to May 1989 and the remaining 7 pounds were removed during the second period of operation from November 1989 through May 1991.

The decrease in chemical mass captured during the second operational period despite increased flow rates is attributed to the reduction in contaminant levels due to groundwater treatment during the previous period.

Soil

The teardrop-shaped FDA soil biotreatment area is approximately 225 by 250 feet. It originally contained approximately 4,000 cubic yards of hydrocarbon-contaminated soil, which was spread evenly over the treatment area and graded to a depth of approximately 3 feet.

The progress of the soil bioremediation was monitored monthly during its operation in accordance with RWQCB requirements and procedures outlined in the O&M Manual. Because bioremediation occurs predominantly in the uppermost one foot of soil, the soil in the biotreatment area was processed in three separate lifts, each approximately I foot thick. When bioremediation of a soil lift was complete, the soil was removed from the biotreatment area and placed in a soil borrow area for construction purposes. One hundred-twenty soil samples from the biotreatment area were collected and analyzed. TPH was detected in 20 of the 120 samples from the biotreatment area, mostly in soil samples collected before treatment system startup in August 1988 and after removal of a lift. During operation of the biotreatment area, TPH concentrations were confirmed to be "nondetect" for several months before lifts were removed. Bioremediation of the first 1-foot lift was accomplished by November 1989 and the lift was removed on November 17, 1989. The second lift of bioremediated soil was removed August 8, 1990. The third and final lift was removed on August 27 and 28, 1991, after the time period discussed herein. The final soil removal in August 1991; completed the soil bioremediation activities at the FDA.

Microbe Population

The results of the analysis of soil samples submitted for microbial analysis are presented in Figure 8. The indigenous microbe population in the soil at the FDA contains a subpopulation of hydrocarbon-utilizing microorganisms (HCUs). The percent of HCUs in the total microbe population has ranged from 0.5 to 100.0 percent in soil samples collected during the monitoring period. For each sampling event, the count of the total microbe population is averaged over the-

four quadrants; the average is calculated the same way for the HCUs. In the calculation of the averages, the HCU count was considered to be 100 percent of the total count if the reported HCU count was greater than the total count. The average HCU population is divided by the average total population to obtain a percentage; these values are then plotted as a function of time.

In general, HCU populations grew steadily after the initial startup and after each lift of remediated soil was removed and unremediated soil was exposed. When HCU populations peaked and declined and a corresponding absence of detectable TPH was observed, soil were considered to be remediated and were removed from the biotreatment area.

SUMMARY

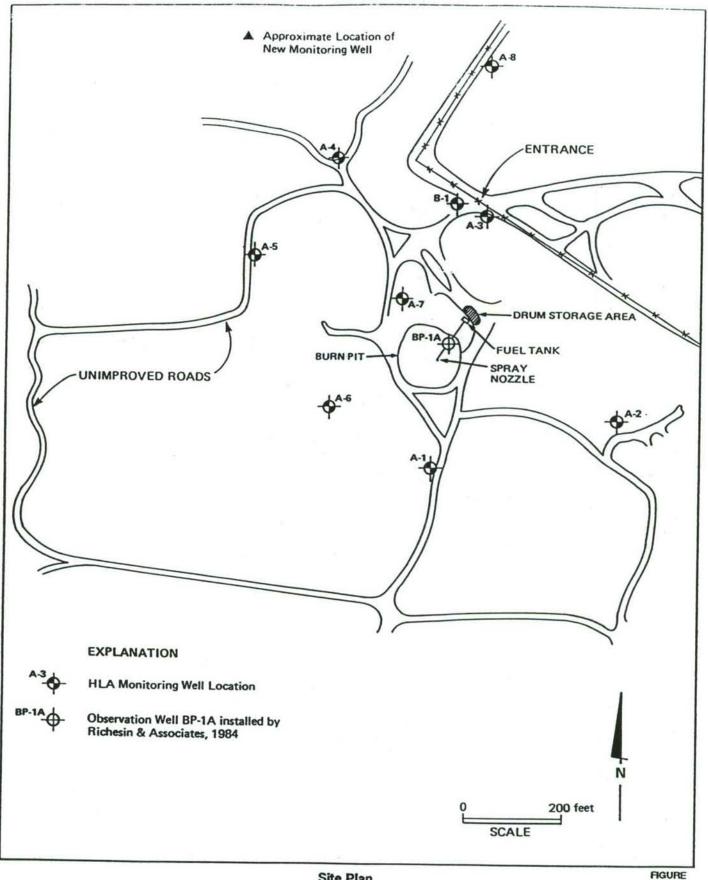
Groundwater extraction at the FDA appears to effectively control groundwater flow in the areas of groundwater contamination. Groundwater flow modeling indicates that the areas of known groundwater contamination are within the zone of capture of the two-well extraction system. The organic chemicals detected in perimeter Wells A-1, A-5, and A-6 are also within this zone of capture.

The groundwater treatment system operated from August 1988 until allowable maximum contaminant levels in the effluent were exceeded; the system was subsequently shut down in May 1989. The system was restarted in November 1989 after design modifications were completed and the first lift of bioremediated soil was removed. Except for minor routine maintenance, the system has been operating continuously since then.

The monitoring program for the treatment system has consisted of sampling and analysis of soil moisture, soil chemistry, soil microbes, vadose zone groundwater, monitoring well groundwater, and treatment system groundwater. Approximately 4,000 cubic yards of petroleum hydrocarbon and solvent-contaminated soil have been bioremediated in three successive lifts. Soil chemical results, in conjunction with microbe population analyses, provided dependable evidence of the complete remediation of each lift.

Analysis of vadose zone pore water samples have indicated that minimal leaching of chemicals had occurred in the biotreatment area. Unidentified hydrocarbons detected in lysimeter samples are most likely nonpetroleum-based hydrocarbons occurring naturally in the biotreatment and excess spray area soil. Hydrocarbons detected did not match the fingerprint of those compounds shown to have occurred at the burn pit and their presence in lysimeter samples outside the biotreatment area suggest that their occurrence is not related to the biotreatment process.

VOC concentrations in groundwater at the FDA have generally decreased since the treatment system startup. Since the initial startup in July 1988, the groundwater treatment system has effectively extracted and treated approximately 17,000,000 gallons of contaminated groundwater as of May 1991. During this same period, approximately 17 pounds of contaminants have been removed through operation of the system. Regularly scheduled monitoring maintenance and GAC canister changeouts have kept the system operating continuously since November 1989.



Site Plan Fritzsche Army Airfield Fire Drill Area Fort Ord, California

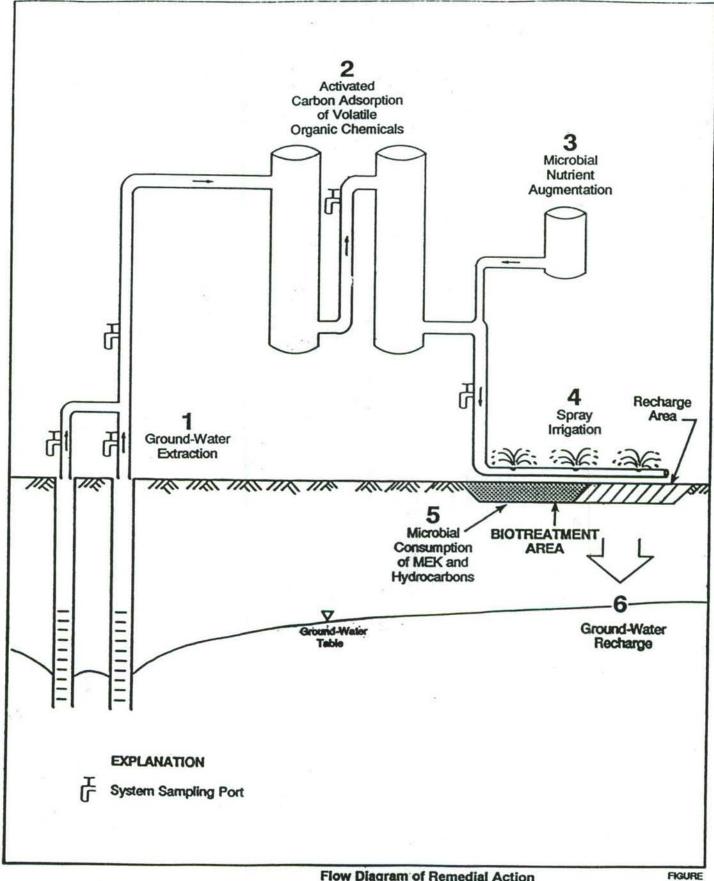


GROUND SURFACE	
cot oot	
60, - 80, Ā	
	A-AQUIFER
110' - 150'	
	SALINAS-VALLEY
	AQUICLUDE
180' = 220	ACCICLODE
	1
	180-FOOT AQUIFER
300, - 320, 3	???
	400-FOOT AQUIFER
	F 14
550' - 650'	
550 - 650	
	AQUIGLUDE
	ACCOLUDE
750	
750	
	900-FOOT AQUIFER
	FIGURE

Geologic Section Fritzsche Army Airfield Fire Drill Area Fort Ord, California

2

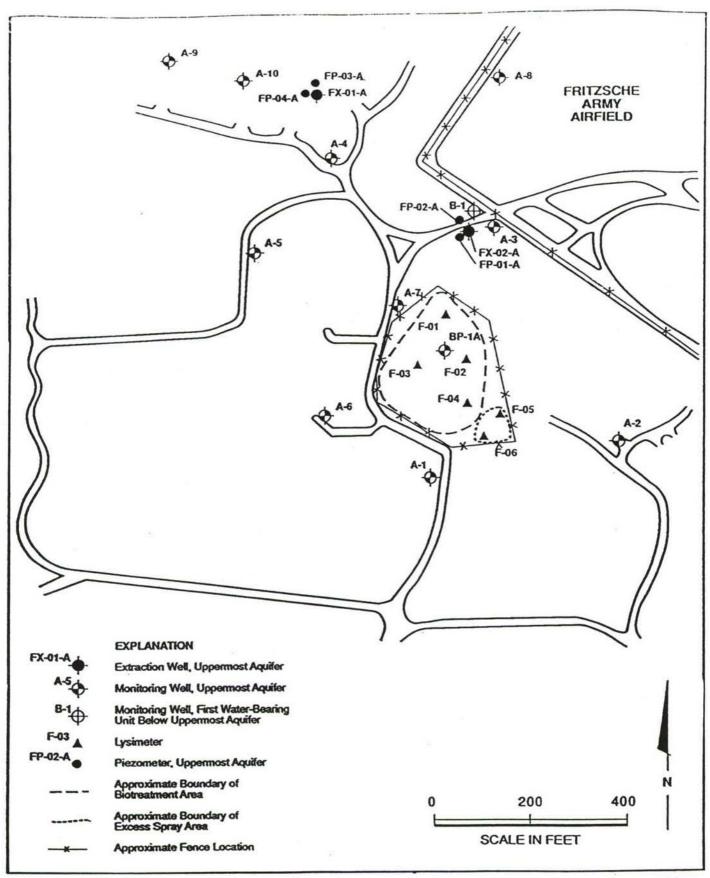




Flow Diagram of Remedial Action Ground-Water and Soil Treatment System Fritzsche Army Airfield Fire Drill Area Fort Ord, California

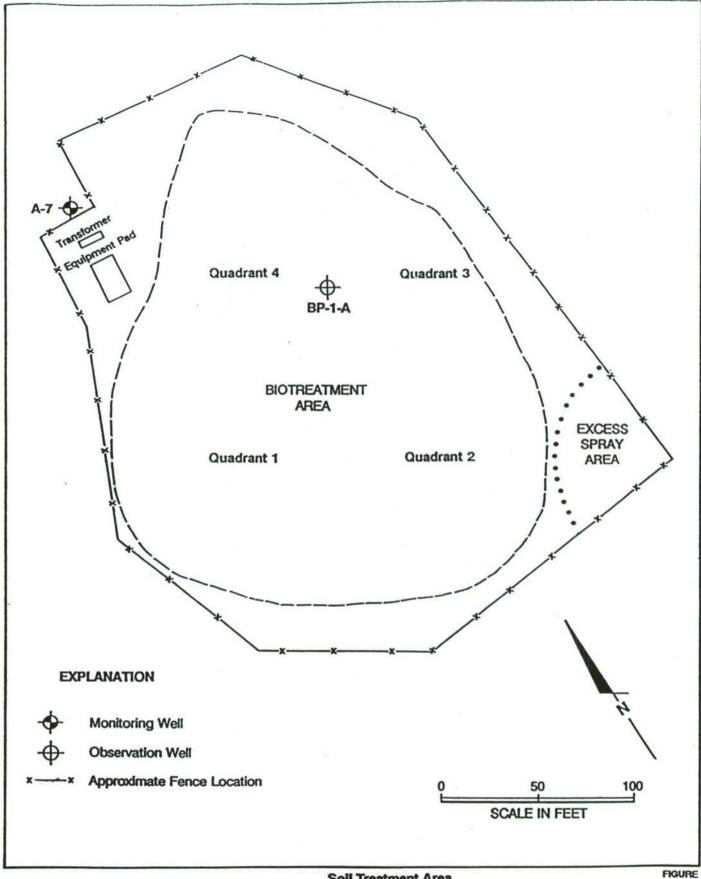
3





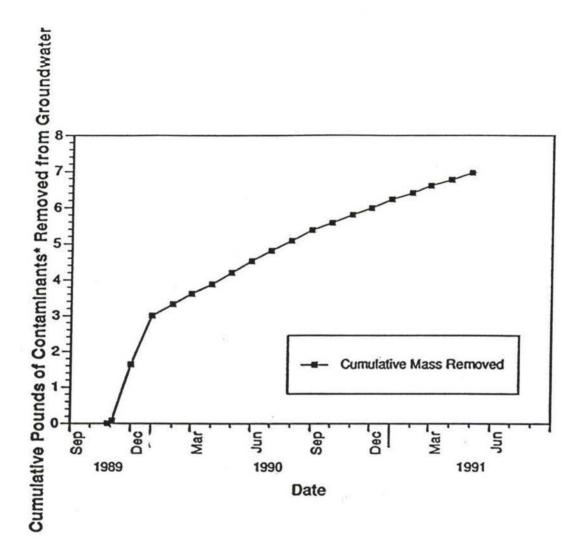
Groundwater and Soil Treatment System Fritzsche Army Airfield Fire Drill Area Fort Ord, California FIGURE





Soil Treatment Area Ground-Water and Soil Treatment System Fritzsche Army Airfield Fire Drill Area Fort Ord, California





NOTE: Approximately 10 pounds of contaminants were removed from groundwater during the previous period of operation (July 1988 through April 1989).

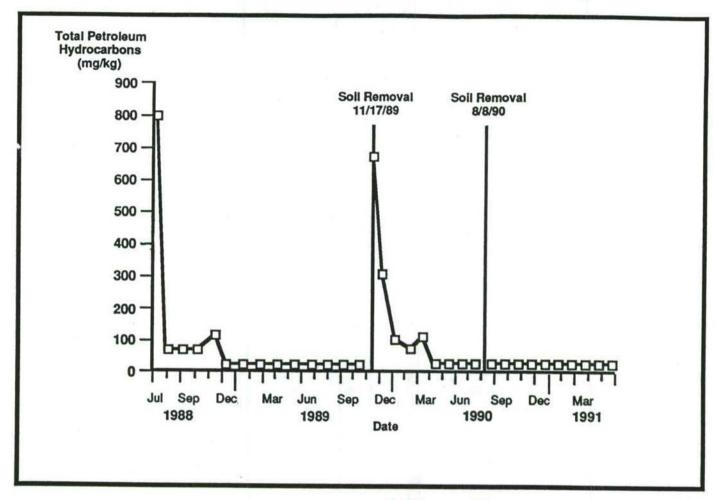
1,1,1-TCA, Total 1,2-DCE, 1,1-DCE, 1,1-DCA, TCE, MEK,PCE, and Chloroform

Chemical Mass Removal Trend Fritzsche Army Airfield Fire Drill Area Fort Ord, California FIGURE





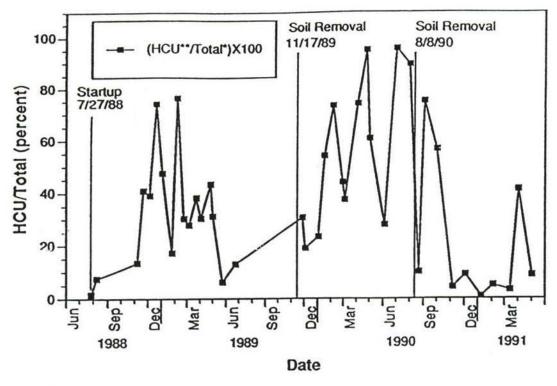
Soil Treatment Summary

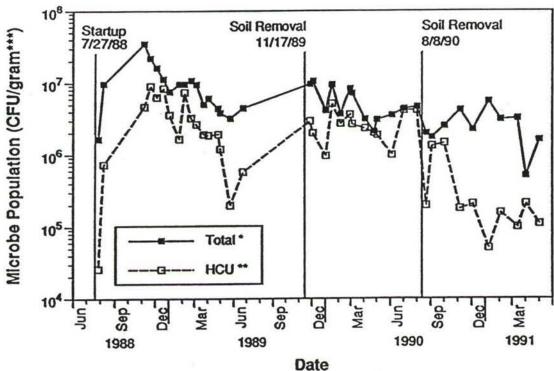


Soil Treatment Summary Fritzsche Army Airfield Fire Drill Area Fort Ord, California

FIGURE

7





NOTE: Population values are expressed as the mean population of all four quadrants.

- * Total microbe population
- ** Hydrocarbon-utilizing microbe population
- *** Colony-forming units per gram of soil, wet weight

Microbe Population Trends, Biotreatment Area Fritzsche Army Airfield Fire Drill Area Fort Ord, California





UNIVERSITY RESEARCH INITIATIVES IN ENVIRONMENTAL SCIENCE

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ABSTRACT

The Army Research Office program in environmental science is primarily directed to the destruction of military toxic wastes (especially chemical agents, explosives and propellants) and the clean-up areas contaminated by these wastes. To strengthen its environmental program, the Office has recently awarded five University Research Initiatives (URIs). These awards are for five year interdisciplinary programs.

Two of the URIs are in the area of use of supercritical water reactors to destroy organic compounds in enclosed chambers and at temperatures well below those required for open burning. One URI will integrate enzymatic, genetic and physiological studies with mathematical analysis to define the factors controlling the rate of biodegradation of military toxic wastes. Another one is directed to the combustion of materials containing phosphorus and other heteratoms with the objective of elucidating conditions associated with the production of undesirable byproducts and of developing means to monitor for their presence. The fifth URI is concerned with the study of contamination of the subsurface environment by fluids immiscible with water; transfer processes in such multiphase systems must be quantitatively described if a understanding of a contaminated site is to be developed.

This presentation will provide a brief overview of the rational and objectives of these URI programs in environmental science.

The proposed URI research program will support development in four areas with high potential for several important Army toxic waste disposal problems, namely, (1) chemical react for destruction of waste; (2) monitoring emissions from incineration of waste; (3) bio- remediation of areas contaminated by waste; and (4) transfer processes in mixed phases (groundwater contamination). "Army toxic wastes" here refers to constituents of chemical and explosive munitions and manufacturing byproducts. The research will be carried out on families of chemical compounds related to the target materials.

The chemical reactor program will emphasize promising technologies for controlled, chemical destruction materials using supercritical water as a reaction medium. Information is needed on properties of supercritical solutions of organic materials related to military toxic wastes, along with salts and metal oxides. Similarly, kinetics and mechanisms of reactions in supercritical water are not well understood. Also of interest are the potential for use and special properties of liquid chromatographic reactors. Other promising destruction media will be considered.

The incinerator monitoring program seeks to provide information on the combustion products from incineration of military wastes and to develop sensitive (ppb level), species-specific probes to identify and measure these products in real time. The program emphasizes continuous monitoring of temperature and species and mapping of the flow-field as well as determination of oxidation products, intermediates, reaction rates and kinetics. The requirement for fast response, high specificity, sensitivity, and spatial resolution may dictate the use of laser based measurements.

Biodegradative Microbiology and Biochemistry will emphasize the demilitarization of obsolete ordnance, wastes from energetic material manufacture, and chemical weapons destruction. Compounds of nitrogen, phosphorus and sulfur must be mineralized. To do this requires identification and characterization of suitable microbes, determination of conditions under which they can thrive, and understanding of mechanisms for potentiating their activity. Investigations will include physiological and genetic control mechanisms involved in biodegradative pathways in bacteria, molecular biology and biocatalytic chemistry of degradation of



compounds representative of military toxic wastes, and limiting factors and kinetics in biodegradation.

Transfer processes in mixed phases address the contamination of subsurface environment by fluids immiscible with water. The subsurface systems are multiphase, including solid, aqueous, immiscible organic, and vapor phases. Multiphase problems are a superset of subsurface flow and transport problems. Among the most important unresolved issues are the effects of measurement scale, system dimensionality, and media heterogeneity on fluid flow, adsorption/desorption processes, and interphase mass transfer processes.

The winners in this URI initiative competition are summarized below, along with their projected funding levels. The next several pages contain abstracts and some additional information on each of the programs in the order shown below.

US ARMY UNIVERSITY RESEARCH INITIATIVE PROGRAM FY 92-96

ENVIRONMENTAL SCIENCES (\$13M/5y):

CHEMICAL REACTORS (\$5.5M):

MIT U Delaware U Texas-Austin J. Tester, Chem Eng M. Klein, Chem Eng K. Johnston, Chem Eng

COMBUSTION PROBES (\$2.5M):

Cornell

F. Gouldin, Mech & Aero Eng

BIODEGRADATION (\$2.4M):

Texas A&M

B. Dale, Ag Chem Eng

TRANSFER IN MIXED PHASES (\$2.5M):

U N Carolina

C. Miller, Env Sci & Eng

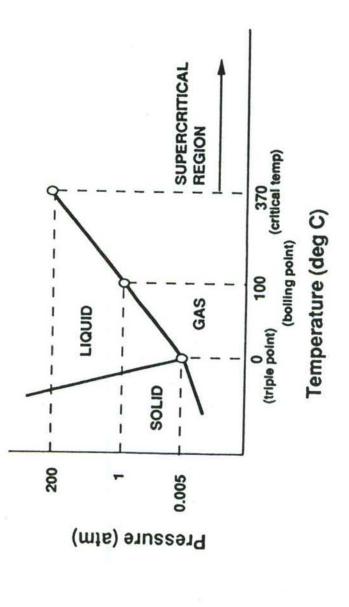
Abstract

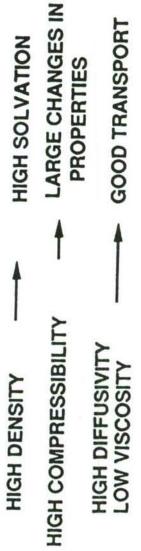
Supercritical water oxidation (SCWO) is a promising and innovative technology for the complete and efficient destruction of toxic military wastes. For toxic compounds containing hydrogen, carbon and nitrogen atoms, the final oxidation products are water, carbon dioxide, and nitrogen. In addition, toxic compounds containing heteroatoms such as chlorine, fluorine, sulfur, and phosphorus can be reacted and neutralized to form insoluble salts as products. These benign chemical reaction pathways are strongly influenced by the physical condition of supercritical water environment which changes markedly over processing temperatures above the critical temperature of pure water (374°C) to about 700°C and at pressures in excess of water's critical pressure of 22.1 MPa Because most organic compounds and oxygen are (3200 psi). completely soluble in supercritical water, and because reaction temperatures are sufficiently high, rapid and complete oxidation with high destruction efficiencies can be achieved in modestly short reactor residence times.

However, commercial design and reliable operation of practical processes require a more complete understanding of several important chemical and physical phenomena that occur during SCWO. They include both molecular-level processes such as oxidation kinetics and mechanisms, solid salt formation, and phase separation and macroscopic phenomena such as fluid mixing, dispersion, corrosion and erosion of materials, and transport-limited chemical reactions. In the proposed work, we intend to study these phenomena in a five-element, experimental and theoretical research program that will (1) measure oxidation rates of model and surrogate compounds, (2) measure salt nucleation and precipitation rates, (3) model phase separations and elementary reaction kinetics, (4) develop techniques for evaluating materials for corrosion performance and (5) develop a engineering process simulator of SCWO of toxic military wastes. Our research team consists of seven principal investigators with broad experience in supercritical water oxidation, applied kinetics, combustion and pyrolytic processes in multi-phase systems, corrosion engineering, and process design and simulation.

A major benefit of the proposed studies will be a better quantitative characterization of SCWO from well-defined experimental measurements and molecular-based modeling of rate phenomena and thermodynamics. In addition, by integrating the results of these fundamental studies of important chemical and physical phenomena into the reactor and process engineering model, we will generate a state-of-the-art simulation code that can be used by others for the evaluation and scale-up of SCWO for treating military toxic wastes.

PRESSURE-TEMPERATURE PHASE DIAGRAM OF PURE WATER ARMY RESEARCH IN SUPERCRITICAL FLUIDS





CHEMICAL REACTORS: SUPERCRITICAL WATER OXIDATION

Massachusetts Institute of Technology:

Experiments:

Global Kinetics of Destruction

Salts - Nucleation and Phase Separation

Corrosion

Modeling:

Reactor Engineering Process Simulation

Target Compounds:

Malathion

DiMethyl Sulfoxide

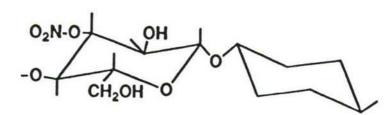
Ammonium Perchlorate

NH₄CIO₄

Nitroglycerine

Nitrocellulose

H₂C-ONO₂ HC-ONO₂ HoC-ONO2



Abstract

Disposal of hazardous waste is a major national problem that is destined to become increasingly severe in the future. Many of the materials of interest to the Department of Defense are especially hazardous or toxic. These materials include explosives and propellants (energetic materials) and chemical warfare agents. Standard methods of demilitarization, such as atmospheric combustion, may trade one potential pollution problem for another. Therefore, there is a need to explore fresh concepts that are technically and publicly more acceptable. One such approach is to carry out oxidative degradation reactions of organic materials in water at temperatures near and above the critical point of pure water (SCW).

Considerable scientific basis underlies this approach. One of the key principles of this technology is that the solubility of organic compounds in water usually changes markedly at high temperature, in part because of the large decrease in the dielectric constant of water with increasing temperature. Non-polar organic molecules are completely miscible in water. Partially polar molecules exhibit sharp solubility increases. Moreover, water near its critical point is sufficiently hot that pyrolysis, hydrolysis, and oxidation rates are fast. Thus the miscibility of reactants and additives (e.g., oxidants, catalysts) is uniquely high at conditions where rates are also high.

These scientific and engineering fundamentals have generated much interest in the commercial use of high temperature water (HTW) in reaction, and in particular, oxidative destruction, processes. The concept of oxidative destruction of molecules has been taken to the commercial point by several companies, but many aspects of the chemistry remain largely a frontier research area. In particular, basic rate data are at a global level and the underlying elementary steps and their associated kinetics have not been resolved. This is due in part to the difficulties encountered in experimental work.

Development of safe and reliable methods to destroy hazardous wastes will require a clear understanding of the chemical and physical phenomena that take place in the reactor. This information will be provided by a combination of in situ FTIR and FT-Raman spectroscopy measurements of the reaction rates and species and off-line product analysis to obtain the mass balance. These data are the inputs to a reaction engineering analysis of the kinetics and physical processes to model the reactor. The reaction engineering model will enable scaling to be made to an industrial reactor suitable for DOD needs.

CHEMICAL REACTORS: SUPERCRITICAL WATER OXIDATION

University of Delaware:

Experiments:

Identify Reactive Intermediates - FTIR,

Raman

Modeling:

Detailed Reaction Kinetics

Target Compounds:

Nitrates

R-C-NO2

Nitrate Esters

R-C-O-NO2

Nitramines

R-C-N-NO₂

Nitrate, Perchlorate Salts NH₄NO₃, NH₄ClO₄

High N Compounds - Azides

Pb(N₃)₂

Abstract

A collaboration between chemists and chemical engineers is uniquely well-suited for addressing multidisciplinary research needs in supercritical water oxidation (SCWO). We will develop a knowledge of the behavior of polar, hydrogen bonding, and acid-base interactions in supercritical water (SCW) solutions containing organic molecules. These molecular interactions will investigated both spectroscopically and theoretically over a wide range in temperature and density. We will use these results to describe solvent effects on reaction rates and mechanisms. mechanistic investigation will be undertaken to specify the routes by which reactive intermediates are generated in supercritical water media. The intermediates will be generated by (a) thermal and photochemical activation on the surfaces of metal oxide dispersions, (b) pulse radiolysis of water to form hydroxyl radicals, (c) photoexcitation of soluble organic compounds which then undergo proton transfer and electron transfer, and (d) electrochemical reactions. Subsequent reaction pathways will be monitored in-situ spectroscopically and electrochemically. the equilibrium and dynamics of proton transfer and electron transfer reactions will be studied, and the role of solvation by SCW will be determined at conditions near and beyond the critical point. A new lattice fluid equation of state for SCW which treats hydrogen bonding will be used to calculate thermodynamic solvent effects on reaction rate constants, in conjunction with quantum mechanical calculations of transition state structures. development of a fundamental understanding of the molecular properties of SCW solutions, and how these properties influence equilibrium and dynamic chemical processes, will be of broad interest in developing SCWO as a practical degradation process.

CHEMICAL REACTORS: SUPERCRITICAL WATER OXIDATION

University of Texas-Austin:

Experiments:

Spectroscopy of charge transfer reactions

Redox Reactions with Metal Oxides

Electrochemistry

Modeling:

Equation of State including H bonding

Solvent effects on Reaction

Abstract

This proposal is in support of the U.S. Army's mission to destroy its stockpile of obsolete chemical weapons by incineration. The primary requirement of this mission is complete destruction of these weapons under conditions of maximum safety to Army personnel and the public. Upset conditions in the incinerator are likely to lead to the emission of undesirable byproducts of combustion. Our objective is to elucidate conditions associated with the creation of undesirable products and to develop means to monitor for their presence.

A focal experiment, conducted jointly by all the principal investigators, has been formulated both to provide reliable data for the development of detailed chemical kinetic models for the decomposition and combustion of CWA simulants and to demonstrate the monitoring capabilities that have been devised. All of the monitoring and diagnostic capabilities to be developed by the group will be applied to this experiment and will use the same experimental test bed.

The required knowledge base for this mission will be provided by a research program in which the incineration of chemical warfare simulants will be studied from the initial attack upon the simulant by small radicals, through the pyrolysis process, and finally, to monitoring of the products of combustion. The initial chemical reactions and their rates will be studied with crossed radical and molecular beams and with the REMPI technique. FTIR studies within a flow tube reactor will be applied to identify the stable pyrolysis products. These methods will also permit identification of reaction intermediates and studies of the behavior during decomposition of the functional groups of which the CWA molecules The final products of combustion will be studied are composed. with color center laser IR spectroscopy using novel techniques whereby the spatial distribution of the combustion products is A detailed kinetic model for the combustion of chemical warfare agents will be developed. In total, these studies will lead to an understanding of the conditions to be maintained within the incinerator for good combustion and to the development of sensitive means for continuously monitoring of the products of combustion as a guide to recognition of the existence of upset conditions.

We recognize the importance to the U.S. of training scientists and engineers with specific skills relevant to the incineration of chemical weapon or other wastes. The nature of the studies we propose, and the many tasks we have identified, are consistent with training 20-30 students at the M.S., M.Eng., and Ph.D. levels. Approximately 40% of the budget is attributable to graduate student

support. We have identified a large number of relevant thesis topics in direct support of our research goals and have listed them in the proposal. Significant technical contacts and collaborations already exist between Cornell faculty and U.S. Army experts. We plan to build upon these contacts both to enhance the opportunities for our students as well as to promote the dissemination of the results we shall obtain.

ACTIVE AGENTS

SIMULANTS

Mustard Gas

VX

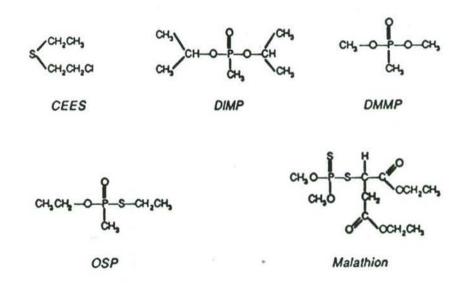


Table 1. Common Chemical Warfare Agents (CWAs) and Model Compounds of Interest as CWA Surrogates for SCWO Studies (Source: Seiders, 1990)

COMBUSTION: KINETIC MECHANISMS & MODELS CORNELL UNIVERSITY

FLOW REACTOR FTIR, GC CWA Pyrolysis, Oxidation (E. M. Fisher) Photoioniza. MS MOLECULAR BEAM CWA + O, H, OH KINETIC (P. Houston) MODEL LAMINAR FLAME REMPI, LIF CWA/hydrocarbon, O2 Molec. Beam/MS (T. Cool) RATE DATA BASE CI,F,N,S,P -> organic framework

COMBUSTION PRODUCT SPATIAL DISTRIBUTION

FLOW REACTOR & FLAME

IR Spectral Signatures

(W. Tsang - NIST)

Color Center

Multiple Line of Sight -

Lasers

MONITOR

Tomography (F. Gouldin, G. Wolga)

Abstract

The principal objective of this research proposal is to integrate fundamental enzymatic, genetic and physiological studies with mathematical analysis to better define the factors controlling the rate of biodegradation of selected model compounds representative of military toxic wastes. the proposal focuses on further developing the biodegradation potential of the broadspectrum organophosphorus hydrolase (OPH) enzyme when used alone, in enzyme-based complexes, as well as in microbial systems in pure cultures and microbial consortia.

It is generally assumed that biodegradation leads to less toxic products; however, the overall toxicity of the biodegradation mixtures may increase during some biodegradation processes. this reason, it is important to completely mineralize toxic waste products or render products completely innocuous. A second key objective is to combine the fundamental detoxification studies mentioned above with precise toxicity measurements and statistical/mathematical analyses of metabolic processes identify those genetic and physiological factors which affect the toxicity of the biodegradation mixtures.

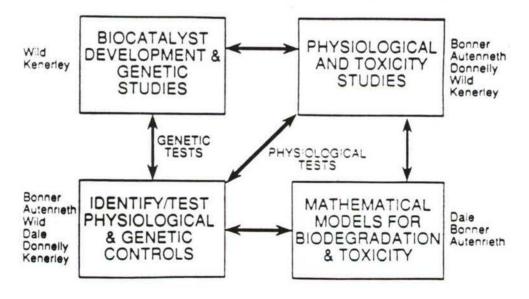
In order to accomplish these goals, the integration of molecular genetics, biochemistry, microbiology, toxicology, and bioengineering disciplines is required to understand and quantitatively describe the molecular, cellular and physical factors controlling the biodegradation of toxic wastes. Interdisciplinary groups with such comprehensive capabilities are rare; however, we have assembled an interdisciplinary group which is able to address the major factors controlling the biodegradation of military toxic wastes in an integrated way.

In the first three years of this project, we will further develop ability to couple the OPH enzyme with the subsequent degradation steps required to totally degrade complex neurotoxins. The enzyme will be utilized in pure microbial culture systems and in microbial consortia capable of degrading both (para-nitrophenol nitroaromatics and trinitrotoluene) organophosphorus compounds or OP fluoridates (parathion, paraoxon Our research in the enzymology and biochemistry of organophosphorus biodegradation is widely recognized, and this expertise will be adapted to encompass the effects of fundamental genetic and environmental factors on the biodegradation kinetics of pure microbial cultures and consortia in aqueous systems. metabolism of the systems will be studied and modeled to identify rate-controlling processes.

The third project objective is to propose and test relevant hypotheses. During the fourth and fifth years of the project, if approved, we will use the increased understanding and experimental capabilities derived from genetic, physiological and mathematical studies during the first three years to propose and test means of 1) increasing the biodegradation rates and 2) decreasing the toxicity of the biodegradation mixtures for these model compounds and microbial systems. We will also extend the capabilities of our microbial consortia by including species capable of degrading mustard compounds.

This proposal represents an integration of disciplines to address the fundamental processes which control the biodegradation and toxicity of military toxic wastes. These biodegradative systems will be broadly applicable to military toxic wastes and we would plan to integrate other microbial or genetic systems as appropriate to address complex bioremediation needs. The intellectual framework we develop for addressing biodegradation and the structure of this interdisciplinary group will also serve as models for other integrated, interdisciplinary biodegradation efforts.

INTERACTIONS OF RESEARCH ACTIVITIES AND INVESTIGATORS



Abstract

Contamination of the subsurface environment by fluids that are immiscible with water is recognized as a commonplace occurrence. Subsurface systems that include immiscible fluids are multiphase systems. The phases present may include a solid, an aqueous, an immiscible organic, and a vapor. Fundamental processes that govern the behavior of such systems are complex, and a considerable research effort is underway to more fully understand these systems. Multiphase problems are a superset of subsurface flow and transport That is, research findings from multiphase investigations often are applicable for groundwater systems that have fewer than four phases. Given the broad nature of the implication of the problems, the present emphasis on multiphase research is appropriate.

Present research efforts not withstanding, several crucial questions remain to be answered for multiphase subsurface systems before a mature level of understanding is achieved. A lack of quantitative knowledge of the effects of subsurface heterogeneity on fluid flow and contaminant transport phenomena in multiphase systems is the limiting factor affecting the development of an improved understanding of such systems, from both a theoretical and applied perspective. Yet, little work has been experimentally, numerically, or theoretically to investigate the effects of subsurface heterogeneity on flow and transport phenomena in heterogeneous multiphase systems.

The proposed project would address the deficiencies in the current level of understanding of flow and transport phenomena in heterogeneous multiphase systems through novel: (1) experimental investigations, (2) numerical model development and application, (3) theoretical analysis, and (4) comparisons among experimental, numerical, and theoretical results. The proposed project will strengthen, but not duplicate, an active ongoing research program in multiphase flow and transport processes, directed by the principal investigator of the proposed project. In addition to the primary benefits derived from this work, the proposed project will: significant existing facilities for investigating multiphase flow and transport phenomena; enhance the existing facilities to provide a unique capability for such study; provide a significant opportunity for training graduate students; and encourage active collaboration by other researchers throughout industry, government, and other academic institutions.

The laboratory phase of research will characterize the macroscopic hydraulic properties (pressure-saturation-permeability relationships) of the chosen fluids and solid phase materials and also measure the sorption-desorption and hydrodynamic dispersion properties. Two (and later three) dimensional models of the porescale density distributions of the fluid in the medium will be constructed so the time/space measurements of fluid migration can be made under controlled conditions. Repeatability of the experiments will be stressed. Small microcosm experiments will examine flow and transport with different porous media in homogeneous and heterogeneous cases.

The mathematical modeling efforts attempt to extend the laboratory measurements to large scale heterogeneities encountered in the field. The PI will extend his 2-D model of multiphase flow to 3-D. Both models will be used to simulate the laboratory experiments. Based on success with modeling laboratory flows, larger areas with prescribed inhomogeneities will be modeled. Those results will be compared to a stochastic model of the same conditions to establish the veracity of the stochastic model. Finally, extensions of the stochastic model to field-type conditions, where heterogeneities of hydraulic properties are not well known, will explore the capability and uncertainty of predicting multiphase flows.

The cellular automata approach to the multiphase problem will also be developed from first-principles and results compared to more conventional methods.

The POC's at the Army Research Office for each of these programs are listed below. Please contact them for further information.

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COMBINING ENVIRONMENTAL MEASUREMENTS AND MODELING WITH BIOLOGIC SURVEILLANCE TO ENHANCE HEALTH RISK ASSESSMENT VALIDITY

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ABSTRACT

Initial short-term environmental monitoring by various groups in Kuwait following the initiation of the oil fires indicated no acute health risk. However, the long-term health impacts, such as chronic effects and increased incidence of cancer were not The U.S. Army Environmental Hygiene Agency (USAEHA) was tasked by the Department of Defense (DOD) to assess the health risk to DOD troops that were exposed to oil fire smoke during their stay in southwest Asia. To determine troop exposure and the resultant health risk several types of sampling were conducted. Ambient air sampling for a variety of metals, organics, and inorganics that were expected to be associated with oil fire smoke in the region were collected. In addition, to assess the dermal and ingestion routes of exposure surface soil samples were collected in the area of the ambient air sampling stations. A third sampling modality conducted was industrial hygiene air sampling to assess the risk to more highly exposed populations of troops engaged in long-term outside work. The sampling results will be subjected to Environmental Protection Agency risk assessment methodology used at "Superfund" sites. Individual risk assessments will be performed at each monitoring/sampling location where troops were stationed. addition, back trajectory modelling using the National Oceanic and Atmospheric Administration's HYSPLIT Model will be used to predict exposure concentrations and conduct risk assessments at troop locations where no sampling was conducted. When conducting the risk assessments an effort will be made to try and separate the risk contributed by the oil fire smoke from the background risk coming from natural metals in the soil and industrial pollution in the region. An additional component of the study was a Biologic Surveillance Initiative. This involved an element of U.S. Army troops that was studied before deployment to Kuwait, while in Kuwait, and upon return to their home base in Germany. An extensive group of sophisticated medical surveillance techniques, that measured actual contaminant levels in the troops and effects at the cellular level, were employed to try and refine the health risk assessment and make it a more scientifically valid study.

COMBINING ENVIRONMENTAL MEASUREMENTS AND MODELING WITH BIOLOGIC SURVEILLANCE TO ENHANCE HEALTH RISK ASSESSMENT VALIDITY

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Introduction.

The destruction of more than 700 oil wells during the conflict in the Persian Gulf region raised concerns about potential health effects to DOD troops and civilians exposed to the oil fire smoke. The initial reports from the area by groups conducting monitoring activities (i.e., EPA, French, Norwegians, and the Kuwait Environmental Protection Department) did not find significant quantities of pollutants of concern (except for particulates, which are naturally high in the region) that would cause acute or chronic health effects. However, the groups conducting the monitoring did stress that the long-term health effects to individuals that were exposed to the pollution could not be determined because of insufficient data. It was the concern with potential long-term health effects to DOD troops and civilians exposed to the environmental contamination that prompted the DOD to initiate this study. At the request of DOD Health Affairs the U.S. Army Office of The Surgeon General (OTSG) was tasked to chair a Tri-service medical working group to evaluate the potential health effects of the oil smoke on DOD personnel. The group consisted of medical personnel from each military service, in addition to representatives from the Veterans Administration, DOD Health Affairs, and the Office of the Deputy Assistant Secretary of Defense for Environment, Safety and Occupational Health. As part of the working groups effort a team from the U. S. Army Environmental Hygiene Agency (USAEHA) was dispatched on 1 May 1991 to collect samples and monitor the health effects in South West Asia.

Project Scope.

This project consisted of three main areas, an environmental monitoring effort, with subsequent health risk assessment, an industrial hygiene sampling study, and a biologic surveillance initiative. Upon their completion the three studies will be integrated to obtain a complete picture of the environmental situation in the gulf region and the resultant health consequences to DOD personnel.

1. Environmental Monitoring. The environmental monitoring study attempted to characterize the concentration of pollutants that DOD personnel were exposed to during their stay



in the gulf region. The period of exposure (i.e., time) and the location where that exposure occurred were very variable for the large number of DOD personnel in-theater (approximately 550,000). As of the end of February there were a total of 605 oil wells on fire and 46 gushing oil. The USAEHA monitoring effort commenced on 5 May 1991 and continued until 3 December 1991. At the start of environmental monitoring there were still 558 oil wells on fire and the data collection continued until all the fires were extinguished on approximately 6 November 1991, and as stated above, continued until 3 December 1991 to obtain one month of background data. The area occupied by troops during their stay in the gulf region was extensive, approximately 880,000 square miles within Kuwait, Saudi Arabia, and Iraq. This made quantification of exposure by troop location very difficult. Therefore, as a starting point for exposure measurement, permanent ambient air monitoring stations were established at four locations in Saudi Arabia and six locations in Kuwait, although two in Kuwait were quickly abandoned due to logistical difficulties. The locations were selected based on the fact they were major sites where DOD troops were stationed long term. augment the fixed location sampling, air modeling will be conducted in conjunction with the National Oceanic and Atmospheric Administration (NOAA), to predict pollutant concentrations at locations and times when no sampling was being conducted. In addition to air monitoring, soil sampling was done at the air sites to insure that all potential exposure pathways and media were evaluated. The data generated from the environmental monitoring activities were used to calculate the exposure point concentrations for the health risk assessments. Risk assessments were conducted for each of the seven permanent air/soil monitoring sites where DOD personnel were located.

- Industrial Hygiene Survey. The industrial hygiene (IH) air survey monitored and characterized occupational exposures of DOD personnel who had potential high risk exposure to oil fire emissions. The IH air sampling was conducted from 3 May 1991 to 17 June 1991 at various locations within Kuwait and Saudi Arabia. The focus was on individuals working outdoors and on worst-case situations within the oil fields next to Kuwait The IH air sampling results were compared to recognized occupational health standards to assess the health risk to exposed individuals.
- Biologic Surveillance. The Biologic Surveillance Initiative (BSI) was conducted to refine the results obtained from the health risk assessment. This was accomplished through collection of objective biologic measurements of exposure and effect in real-time and seeking to establish the presence of any observable biologic effect or marker of exposure to oil fire pollutants in a cohort of U.S. soldiers. When an element of U.S. troops was identified that would deploy from Europe to Kuwait and return, a team from USAEHA and cooperating agencies was assembled to plan and carry out a study that would measure the effects of

the oil fires on the troops. The troop unit, the 11th Armored Cavalry Regiment (11th ACR), was given questionnaires, had biologic fluids (blood and urine) collected for analysis, and had pulmonary function tests performed between 1 June 1991 and 14 October 1991. These activities were performed in Germany (prior to deployment to Kuwait), in Kuwait (following exposure to the environment), and upon return to Germany. Following an analysis of the data, the results from BSI and the health risk assessment (HRA) will be compared and integrated. The predictive results from the HRA (which were generated from environmental data) will be compared to the BSI results from actual biologic samples of potentially exposed troops. This comparison will either lend validity to the HRA or show that its predictions are too conservative or not conservative enough.

Risk Assessment.

The methodology selected for the risk assessment is EPA guidance developed for Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) sites, also known as "Superfund". The calculations result in a quantitative estimate of health risk based on the contaminant concentrations and the site exposure characteristics. Assessments conducted using Superfund guidance are based on the reasonable maximum exposure (RME) scenario. The RME is defined as the highest exposure that is reasonably expected to occur at the site. The methodology does not use the absolute worst case scenario, but is nevertheless very conservative in the data that is selected for use and the exposure and risk factors that are incorporated into the assessment. The result of this is the production of risk numbers that generally overestimate health risk by several orders of magnitude. The risk assessment has six distinct steps which will be discussed below.

- 1. Data Collection. The collection of an environmental data base is the heart of any risk assessment. An early determination of the types of data that will be required to complete the risk assessment is essential. Items such as contaminant identities, environmental fate, transport, and persistence of contaminants, characteristics of the source, and contaminant concentrations in the key exposure pathways are required for a quality data base. As with risk assessment, data collection has certain key steps that must be accomplished.
- a. Review of available information. The initial step in formulating data needs is to review the available information on the site characteristics (i.e., climate, topography, contaminant sources), hazardous substances to be monitored (i.e., crude oil analysis, products of incomplete combustion, breakdown products), and identify potential exposure pathways.

- b. Defining Background Sampling Needs. Background sampling is conducted to distinguish site-related (oil fire) contaminants from naturally occurring or other non-site-related levels of chemicals (industrial/vehicle emissions). This was a particularly difficult task for this study due to the large and diverse geographical area covered by the study, the very complex and varied nature of the contaminants produced by the fires, and the large number of sources contributing background contaminants to the area.
- c. Preliminary Identification of Potential Human Exposure. This area of data collection involves determining the following: environmental media that may be contaminated and to which individuals may be exposed and/or through which chemicals may be transported to the potential receptors; areas of concern (i.e., locations where the environmental media is to be sampled); types of contaminants expected at the sampling sites and their environmental behavior, persistence, and accumulation; and potential routes of contaminant transport through the environment.
- d. Developing an Overall Strategy for Sample Collection. In developing a sampling strategy that will adequately address the questions the risk assessment is trying to answer the following factors must determined: sample size, sample location, and sample type.
- e. QA/QC Measures. The QA/QC issues that need to be addressed in the data collection plan are: sampling protocols, sample collection devices/equipment, QC samples, collection procedures, and sample preservation.
- 2. Data Evaluation. After all the environmental samples have been collected and analyzed the data set that is produced must be evaluated to determine its suitability for incorporation in the risk assessment. To evaluate the data and prepare a data set for the risk assessment the following must be accomplished: evaluate the analytical methods, evaluate the data with respect to QA/QC parameters (i.e., blanks, data qualifiers, quantitation limits, holding times), evaluate tentatively identified compounds, compare potential site-related contamination with background, and evaluate the chemicals to be carried through the risk assessment.
- 3. Exposure Assessment. The exposure assessment portion of the risk assessment attempts to estimate the type and magnitude of exposures to the chemicals of potential concern that are impacting the receptor populations. The exposure assessment consists of the following:
- a. Characterization of the Exposure Setting. In this step the physical environment is characterized (i.e., climate, meteorology, soil type, topography) along with a

characterization of the potentially exposed populations (i.e., location relative to the source, activity patterns, and sensitive subgroups).

- b. Identification of Exposure Pathways. This step of the exposure assessment identifies the pathways (i.e., air, soil) by which the previously identified populations may be exposed. The determination of complete exposure pathways involves the following: identify contaminant release sources (i.e., oil fires and lakes) and receiving media (i.e., air and soil); evaluate fate and transport in release media; identify exposure points (i.e., population contact points with contaminants) and exposure routes (i.e., ingestion, inhalation, and dermal contact).
- c. Quantification of Exposure. In this step the risk assessor quantifies the magnitude, frequency, and duration of exposure for each identified pathway. This process occurs in two steps:
- (1) Estimation of Exposure Concentrations. This step of the process involves determining the concentration of contaminants that will be contacted over the exposure period. Exposure concentrations can be estimated using monitoring data (as will be done in this risk assessment) or using chemical transport and environmental fate modeling (as will be for troop areas where no monitoring was conducted). The EPA methodology for Superfund uses the reasonable maximum exposure for each pathway. This value is the 95 percent upper confidence limit of the arithmetic average of the monitoring data for the pathway being evaluated. This methodology develops a conservative exposure concentration, while not using the maximum concentration detected which would not be reasonable.
- (2) Calculation of Intakes. In this step of the exposure quantification the chemical-specific exposures for each identified pathway are calculated. Exposure estimates are expressed in terms of the mass of substance in contact with the body per unit body weight per unit time (e.g., mg chemical per kg body weight per day, also expressed as mg/kg-day). Chemical intakes are calculated using equations that include variables for exposure concentration, contact rate, exposure frequency, exposure duration, body weight, and exposure averaging time. There is a different equation for each exposure pathway/route (i.e., ingestion of soil, dermal contact with soil, inhalation of airborne chemicals, etc.).
- 4. Toxicity Assessment. The purpose of the toxicity assessment is to determine the potential for each chemical of concern to cause adverse effects on the exposed populations. In addition, if possible, to ascertain the relationship between the extent of exposure to a contaminant and the increased likelihood and/or severity of adverse effects. The toxicity assessment is

accomplished in two steps: hazard identification and doseresponse. Hazard identification is the determination of whether exposure to a contaminant can cause an increase in the incidence of a particular health effect (i.e., cancer, birth defect) and whether the adverse health effect is likely to occur in humans. Dose-response evaluation is the process of characterizing the relationship between the dose of the contaminant administered or received and the incidence of adverse health effects in the exposed populations. The types of data considered in toxicological assessments come from human epidemiologic studies and work place exposures, animal studies, and supporting metabolic/physiologic studies. The toxicity assessment is conducted for both carcinogenic and noncarcinogenic effects. When assessing carcinogenic effects the critical toxicity value is the slope factor which estimates the upper bound probability of a response (cancer) per unit intake of a chemical over a lifetime. Another important factor when assessing cancer risk is the weight-of-evidence classification. This EPA system groups chemicals based on the available toxicity data as to their status as human carcinogens (i.e., human carcinogen, probable human carcinogen, etc.). For assessing noncarcinogenic effects the most often used critical toxicity value at Superfund sites is the reference dose (RfD). The RfD is an estimate (with uncertainty of an order of magnitude or greater) of a daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a specified period of time. There are different RfDs for different periods of time [i.e., chronic (lifetime), subchronic (two weeks to seven years), etc.]. In addition to time periods for RfDs, both slope factors and RfDs are derived for the specific route of exposure (i.e., inhalation and ingestion, no RfDs or slope factors are available for the dermal route of exposure). The EPA has listed a hierarchy of sources for toxicity information used in Superfund risk assessments and these were used throughout this study.

5. Risk Characterization. The risk characterization is the final step in the baseline health risk assessment process. In this step the toxicity and exposure assessments are integrated into quantitative and qualitative expressions of risk. To characterize potential noncarcinogenic effects, comparisons are made between projected intakes of contaminants and toxicity values (RfDs). Potential carcinogenic effects (i.e., probabilities that an individual will develop cancer over a lifetime of exposure) are estimated from projected intakes and chemical-specific dose-response values (slope factors). In accordance with EPA guidelines, intakes for estimating carcinogenic effects are averaged over the receptor populations lifetime, while intakes for estimating noncarcinogenic effects are averaged over the actual exposure period.

- Cancer Risk. Excess lifetime cancer risks are obtained by multiplying the intake rate at the exposure point of the contaminant by its cancer slope factor. Under the Superfund Program, the EPA has determined the acceptable range of excess cancer to be 1 \times 10⁻⁴ to 1 \times 10⁻⁶ (i.e., the probability of one excess cancer in a population of 10,000 to one excess cancer in a population of 1,000,000, respectively, under the conditions of exposure). A risk level of 1 X 10⁻⁶, representing a probability of one in 1,000,000 that an individual could develop cancer due to an exposure to potential carcinogens at a site, is often used as "the point of departure" by regulatory agencies to trigger The total cancer risk for a site is generally determined by adding the individual cancer risks for each chemical in the pathways and then summing the risk for all the pathways. there are known synergistic and/or antagonistic relationships between carcinogens or specific target organs are involved these factors can be taken into account when determining cancer risk.
- b. Noncancer Risk. Noncancer hazards are obtained by dividing each chemicals daily intake by its RfD (for this assessment the subchronic RfD, because exposure duration was between two weeks and seven years). These hazard quotients (HQ) are summed for the various contaminants to obtain a hazard index (HI) for the pathway. The HIs for the various pathways are then combined and this represents the total noncancer risk for the site. Under the EPA Superfund Program a hazard index of unity (1) is considered the threshold of concern. As with cancer risk the combining of HIs and HQs can be modified by specific toxicological information such as mechanism of action or effect.
- 6. Uncertainty Analysis. Uncertainty analysis is a key modifying element of any risk assessment. The uncertainty analysis discusses those issues and factors that are not completely understood or known. These issues may cause the assessment to either over or underestimate risk. Issues such as: were sufficient environmental samples collected to adequately characterize the media being evaluated; or using dose-response information from animal studies to predict effects in humans. Some uncertainty factors overestimate risk, others underestimate risk, while some may be capable of doing either under different circumstances. Uncertainty analysis should discuss in detail all issues that may cause risk to be over or underestimated.

The predictive numerical results of the risk assessment will then be used to make some decision concerning the need for site remediation or if a population is at significant risk and should be monitored.

Biologic Surveillance.

Biologic surveillance attempts to look at an environmentally exposed population and asscertain thru direct measurements of



- exposure (i.e., blood and urine analysis) and effect (i.e., pulmonary function testing) if an impact has occurred on that population. The biologic surveillance employs several tools for assessing health effects which may be related to oil fire pollution. These include:
- 1. Pulmonary function testing was performed on the surveillance population (the soldiers of the 11th ACR) to measure Forced Vital Capacity and Forced Expiratory Volume over one second. These parameters were chosen as those indicative of obstructive changes that may occur in the short term due to some anticipated oil fire plume components.
- 2. Medical treatment facility use was monitored by medical components of the 11th ACR. This may reveal population trends reflecting health effects due to pollution.
- 3. Soldiers of the 11th ACR completed questionnaires which ask past and present health history, past and present exposures of interest in the oil fire environment, and psychosocial information which may afford insight into events the other data may describe.
- 4. Direct measures of exposure were also a component of the biologic surveillance. These include trace metals analyses, DNA-adduct and Sister Chromatid Exchange (SCE) frequency assays, and the measurement of volatile organics in serum.
- a. Trace metals analyses will afford a picture of exposure to these elements over the time of deployment. The metals assayed include nickel and vanadium, present in Kuwaiti crude oil. They also include lead, cadmium, copper, iron, arsenic, and manganese. These are being performed on blood and urine at the Armed Forces Institute of Pathology (AFIP).
- b. There are two tests for evidence of genotoxicant exposure incorporated into the biologic surveillance. The first is a very specific test for the presence of covalent adducts of DNA with polycyclic aromatic hydrocarbons (PAHs). This test is being performed through cooperation of Microbiologicals, Incorporated in Rockville, Maryland, and the National Cancer Institute (NCI), National Institutes of Health (NIH), Bethesda, Maryland. A companion test of genotoxic effects (SCE frequency assays), which is very nonspecific, but extremely sensitive, has been conducted at Microbiologicals, Incorporated. These two tests may yield a qualitative picture of gene damage from oil fire pollutants.
- c. A last test of exposure is quantitative in nature. This is a battery of assays for volatile organic compounds (VOCs) in serum. These have been conducted at the Center for Environmental Health and Injury Control, Centers for Disease Control. These tests will depict the exposure to

volatiles of the soldiers tested. This may reveal specific data to contrast with the environmental data, compound by compound, in semiquantitative fashion.

d. Urine from the soldiers who had the genotoxics tests performed will be analyzed at the National Cancer Institute for metabolites of polycyclic aromatics. These analyses may also reveal specific data to contrast with the environmental data, compound by compound, in semiquantitative fashion.

Incorporation of Biologic Surveillance Information into the Health Risk Assessment.

The BSI is an assessment of health effect and exposure through surveillance that provides substantial information in its own right. However, its utility in the setting of the Kuwait oil fires' contamination is greatest in the application of its results to the health risk assessment. The following discussion elaborates on the conceptual and practical match of the two projects. The results of the BSI are coupled with the component results of the HRA three ways:

- 1. The biologic measurements of contaminants in body fluids can be employed in comparison to ambient concentration measurements and dose estimates.
- a. The Exposure Assessment phase of the HRA generates concentrations of contaminants expected to have been present at a site. Biologic measurements of contaminants (i.e., in serum or plasma) can be compared to these modeled environmental concentrations and to actual measurements of the same contaminants. Comparisons can be done several ways:
- (1) For a few substances, literature supports extrapolating from biologic concentrations to environmental concentrations that must have been present. In this way, the concentrations can be directly compared. This is limited to very few chemicals (polycyclic aromatics are one category), and has validity only within certain concentration ranges.
- (2) Other substances can be compared only in an allor-none fashion; that is, the presence or absence of contaminants in soldiers' body fluids may corroborate or deny the environmental concentrations measured or modeled concomitantly.
- b. The Toxicity Assessment phase of the HRA employs specific assumptions to generate predicted outcomes from the modeled concentrations generated in the Exposure Assessment phase. Among these assumptions are some regarding uptake and dose of ambient contaminants. Measured body fluid concentrations may reflect dose and be used in comparison to estimated figures. This may corroborate or deny modeled results.



- 2. Biologic effects measured in soldiers (genotoxic assays, pulmonary function, symptom review) may be used in review of exposure and toxicity assessment. A departure from "normal" or baseline physiologic function that is revealed by measurement may be compared with predicted toxicities. This may serve, again, to corroborate or contradict modeled results.
- 3. Information from questionnaires and diaries may be used anecdotally to corroborate modeled concentrations of contaminants.

The overall impact of the BSI will hopefully be to refine the results of the HRA and present a more realistic look at the health impact of the oil fires on DOD troops and civilians.

Need for Additional Investigation.

Regulatory agencies and responsible parties realize the uncertainties associated with the risk assessment process and the inherent conservatism built into the methodology. They also realize the multi-million dollar environmental clean-ups and regulatory programs that are driven by the results of the risk assessment process. To help refine the health risk assessment process and reduce the uncertainties, the EPA is beginning to focus research efforts on biomarker research. The initial efforts will concentrate on measures for exposure evaluation in human tissues, fluids, and breath samples. Much of the clinical and chemical technology for these studies is already available and hopefully progress will be made to eliminate much of the uncertainty from the risk assessment process and decisions will be based on solid scientific facts not guess work.

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MINIMALLY INVASIVE ENVIRONMENTAL SITE ASSESSMENT

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ABSTRACT

Development and adoption of faster, more reliable, and less costly methods of environmental site characterization are required in order to support an efficient environmental restoration effort. Applied Research Associates, Inc. (ARA) under funding from the U.S. Department of Energy's Environmental Restoration and Waste Management Research, Development, Demonstration, Testing and Evaluation (RDDT&E) Program, has developed a site characterization system which posesses these attributes in comparison to current approaches.

The ARA system combines state-of-the-art site surveying tools with on-site analytical capabilities to enhance the knowledge gained from those tools. Surface geophysical surveys and subsurface exploration are performed in a coordinated effort, rather than as separate, divided programs.

The subsurface exploration is performed using electric cone penetrometer testing (ECPT) in which instrumented rods are hydraulically pushed into the soil. This method allows faster advance, while causing significantly less disturbance around a small hole (1.4-in diameter) compared to drilling, and also transports minimal amounts of material to the surface. ECPT provides fine detail of subsurface character as several physical and geophysical parameters are measured during advance. Soil, soil water, and soil gas samples may be retrieved at selected intervals. A special design allows grouting of the penetration hole during withdrawal.

These data are recorded and interpreted using on-site computers. The results are transferred to an on-site work station. A relational database possessing calculational and advanced graphics allows rapid turn-around of data visualization. An ongoing review allows cross-referencing and correlating of results from contributing measurements. This approach enhances the knowledge gained from all tools and allows for a dynamic, "proactive" site survey based on the expanding database.

This paper discusses a case study demonstrating the application of this approach to site characterization.

INTRODUCTION

Environmental cleanup is clearly the engineering challenge of the '90s. The magnitude of this problem has prompted the Department of Energy (DOE) to initiate the Environment Restoration and Waste Management Research, Development, Demonstration, Testing, and Evaluation (RDDT&E) Program. The goal of this program is in finding faster, better, safer, and cheaper methods of accomplishing this massive cleanup. The research reported herein was funded under that program.

Fundamental to the design of a cleanup strategy for any site is the characterization of the subsurface stratigraphy and the nature and extent of contamination. This is currently done using surface geophysics, drilling and sampling, and monitoring wells. The geophysical investigations are usually directed at obtaining the general character of the subsurface geology and, in some cases, preliminary information on the location of the contaminant. This information is used in planning the drilling and sampling program conducted by a second contractor. The borings are generally laid out in a regular pattern, with the spacing based on engineering judgment. Samples thus obtained are delivered to a testing laboratory for analysis, taking from a few weeks to several months to complete. Data gaps are identified, and a second phase of drilling and sampling is performed. The resulting site assessment provides the basis for determining monitoring well locations.

This conventional procedure is plagued by the lack of interactive analysis of the data from the various sources, inherent slowness and cost of drilling and sampling, the time and cost required for laboratory testing, and the lack of real-time decision making capability. The Minimally Invasive Three-Dimensional (3-D) Site Characterization approach overcomes these shortcomings, resulting in a faster, cheaper, better, and safer site characterization strategy.

The heart of the methodology is the electric cone penetrometer test (ECPT). The ECPT provides a rapid, minimally invasive method for obtaining: 1) a detailed description of the site stratigraphy, 2) ground truth data to enhance the understanding of surface geophysical data, 3) samples for analysis of contaminant concentration, and 4) the ability to place short-term monitoring wells. The ECPT is combined with appropriate surface geophysical techniques (electrical resistivity and seismic reflection for the sites discussed in this paper), and a relational database and graphical presentation code to provide an interactive, adaptive site assessment procedure.

DESCRIPTION OF THE APPROACH

Electric Cone Penetrometer Test

The cone penetrometer has been used for almost half a century in foundation explorations. The ECPT is the best available method of obtaining continuous, fine detail of stratigraphy (Ref. 1), and does so at a rapid rate. Additionally, it produces no drilling spoils, thus reducing or eliminating the waste disposal problem inherent in drilling and sampling, and reducing the exposure of operators to hazardous materials.

Hydraulic rams are used to push a 3.57-cm diameter probe into the ground at a constant rate. Figure 1 is a schematic of a standard probe. The probe carries a number of instruments. The basic measurements are the stresses on the 60° conical tip and the 150-cm² friction sleeve. A porous filter just behind the tip allows measurement of the pressure in the pore water during the penetration. These three measurements may be used to interpret the subsurface stratigraphy (Ref. 2) and to calculate the strength parameters of the soil (Ref. 3 and Ref. 4). A continuous profile as shown in Figure 2 is obtained. Data are recorded every 2 cm providing very fine detail. Weak or strong layers



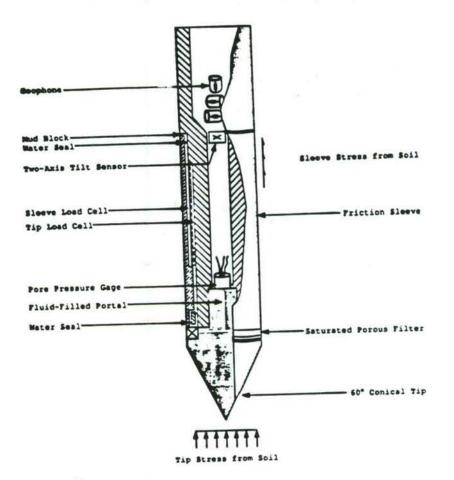


Figure 1. Schematic of ARA Cone.

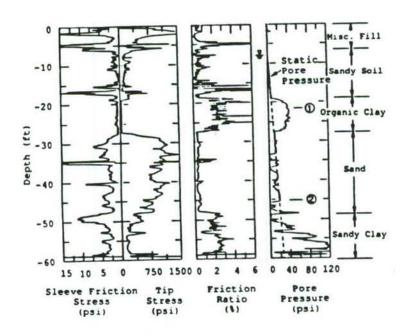


Figure 2. Typical CPT Data.

may be traced from location to location. Some units are very thin layers which most likely would not be identified by drilling.

The pore pressure gage is an excellent indicator of the water table location and can be used to support soil classification. Pore pressure dissipation tests can be used to calculate permeability in fine-grained soils (Ref. 5).

Newer additions to these standard measurements are the downhole seismic system and the electrical resistivity module. The seismic system consists of a three-component geophone inside the probe, and shear and compressive wave sources at the surface. Figure 3 illustrates a typical set of shear wave data produced by alternating the direction of the input force to produce 180° polarized shear waves, which facilitates arrival time determination.

A resistivity probe capable of measuring the resistivity (or conductivity) of the soil matrix is shown in Figure 4. Conductive zones could identify high salts or metals content in groundwater; resistive zones could identify solvents.

In addition to downhole sensors, samplers are available to take soil, soil water, and soil gas samples. These allow testing for contaminants without installing a monitoring well.

Seismic Reflection Surveys

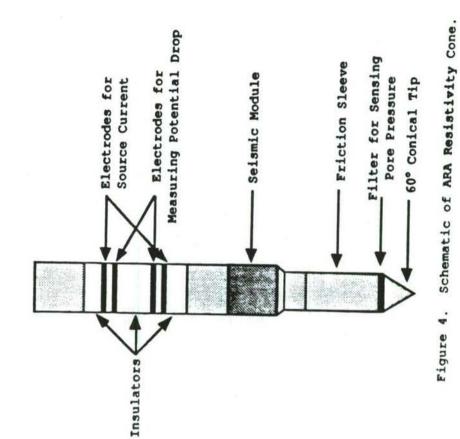
One surface geophysical method which is very complimentary to the ECPT is seismic reflection. Reflections of seismic waves occur at material interfaces due to differences in material stiffness and density. High resolution seismic reflection can map subsurface features such as buried channels, faults, and layer boundaries over large areas.

Standard analysis of reflection data produces time-based sections with no direct measure of layer depths or seismic velocities. ECPT seismic measurements at specific locations along a reflection line provide these wave speeds and layer depths. The resulting data can be used as truth data to the reflection analysis allowing conversion of the time sections to depth-based sections. This procedure facilitates mapping of major features of the site which will effect ground water flow and contaminant transport.

Surface Electrical Resistivity

Surface electrical resistivity surveys produce information on site electrical characteristics. Mineralogical composition of soils, and type and concentration of materials in the ground water effect electrical resistivity. Surface resistivity surveys provide apparent resistivity values representing the integrated resistivity of the entire volume of material affecting the measurement. Successively increasing spacing of electrodes sample successively greater volumes of material centered about the sounding point. Inversion modeling of these data provide best estimates of the resistivity profile at the sounding point. Unfortunately, subsurface variability can effect the solution, reducing the confidence that the inversion profile is an accurate representation of the sounding location.





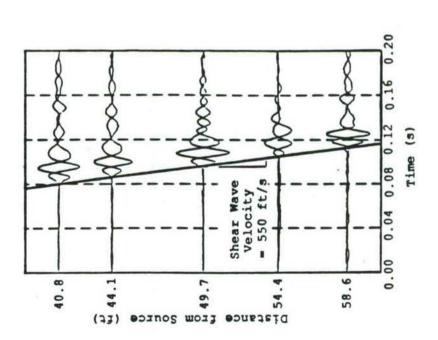


Figure 3. Typical Shear Wave Data.

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The ECPT, on the other hand, provides accurate detail of the profile, directly measuring data downhole during advance. The result is a high confidence description of hydrogeologic features, such as the location of ground water, to be used as ground truth against the inversion profile and reduce the uncertainty in the surface resistivity model. A synergism results from the ability to combine these high confidence data with a surface reconnaissance tool to provide rapid confident electric mapping of a site.

Database

The field database/graphics package is the third element in the modern site characterization approach. Combining the survey results into a relational database scheme allows for numerical modeling and data/model visualization outcomes of the separate survey tools. The results can be readily compared and correlated to reduce the uncertainties or unknowns in the respective survey results.

TECHBASE, by MINEsoft, Ltd. of Lakewood, CO, was chosen to perform these functions. TECHBASE is a relational database which allows for univariate and multivariate statistical analysis of stored data. System graphics include statistics graphics, data plotting, contouring, cross-sections, perspective views, and vector drawings. Point estimator methods include trend surface, triangulation, polygonal, and minimum curvature in two dimensions, and inverse distance and kriging in both two and three dimensions.

Strategy

Having a single, coordinated, and synergized field exploration program improves the site assessment strategy. Conduct of the surface geophysics and ECPT work simultaneously and interactively helps to resolve apparent discrepancies between the data sets, and allows decisions regarding locations of survey lines, ECPTs, and sampling based on a current interpretation of all of the site data. The decisions are expedited by use of an in-field database and visualization code. As additional data are gathered, the interpretations are updated, and the exploration plan is modified as is appropriate.

This approach will result in an optimal assessment of the subsurface stratigraphy, groundwater conditions, and plume location. Further, monitoring well locations will be maximized. It has been estimated that about half of the monitoring wells at a particular site can be eliminated based on ECPT exploration alone, and that the cost savings after including the cost of the ECPT survey can range between 25% and 35% (Ref. 6).

EXAMPLES OF THE SYNERGISTIC APPROACH

Two examples of the application of the synergistic site characterization approach are presented here. These represent the first applications of this approach. The first site, the Bethel-Royalton Landfill, was selected for a limited evaluation of the synergism between the surface electrical resistivity survey and the ECPT. The second site, the Homestake Partners site, was an evaluation involving seismic reflection, surface resistivity, and ECPT measurements.



Bethel-Royalton Landfill Survey

Prior investigations of the Bethel-Royalton, VT, Landfill identified ground water in the surface soil unit which is thought to be transporting contamination. This site provides a hydrogeologic situation (soil saturated with contaminated water) which should be identifiable by electrical resistivity measurements, both surface and ECPT, and by other ECPT measured parameters, most notably pore pressure.

Wenner array soundings were conducted at four locations along a survey line downstream from the landfill. These data were analyzed using the RESIX-Plus computer code by INTERPEX Corporation.

One ECPT was performed at each Wenner sounding point. Figure 5 shows a representative suite of data for one of these penetrations, BR01C, as rendered by TECHBASE. The ECPT survey included tip resistance, sleeve resistance, pore pressure, and electrical resistivity. Of particular interest is the correlation between the hydrostatic rise in pore pressure, indicating the encounter of the water table, and the rapid reduction in resistivity, indicating encounter of a more conductive layer, often related to the presence of ground water.

Figure 6 illustrates how the ECPT resistivity and surface resistivity compare. ECPT tip resistance and ECPT resistivity are plotted along with inversion results of surface data. No ECPT resistivity data were measured for penetration BR05C. Except for BR01C, the "X" for each location denotes CPT refusal depth. Existing data suggest a deep, buried ravine at BR01C, and penetration at that location to refusal was not deemed necessary to the objectives of this phase of testing. This data presentation shows that the surface resistivity and ECPT resistivity amplitudes are in excellent agreement, but that they do not in every case agree on interface location. Specifically, sounding inversions BR01E and BR03E predict a lower water table than is evident from the ECPT data, and all sounding inversions predict a deeper bedrock depth than was encountered by the ECPT. (The surface sounding spreads did not reach sufficient spacing width to locate the deeper layer for BR01E.)

The surface resistivity is a 3-D measurement. The subsurface topography between soundings BR01E and BR02E is quite steep, as evidenced by the penetration depths of BR01C and BR03C (later penetrations between BR01C and BR03C demonstrated that nearly all of the relief occurs very near to BR01C). The intermediate spacings for BR01E were most probably influenced by much shallower bedrock depths than exist at and near the actual sounding location. The resulting inversion would be influenced by the higher resistivity material, implying a greater apparent depth to water table. A similar effect is apparent between soundings BR03E and BR04E. Sounding BR02E, in a flat subsurface terrain area predicts an interface at the same depth as the ECPT resistivity interface. The location agrees with the water table depth located by ECPT pore pressure data.

Further interpretation can explain the inconsistency between the second sounding interface and the ECPT refusal depth. Inversion location of this interface is a fairly consistent depth below refusal. It is possible that ECPT refusal is at the top of a fractured or rubbleized zone rather than at

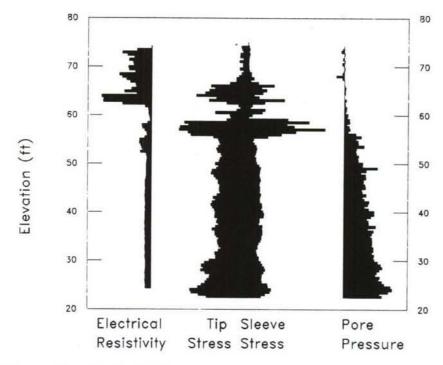


Figure 5. Typical ECPT Data from Bethel-Royalton Landfill Test Site (Penetration BRO1C).

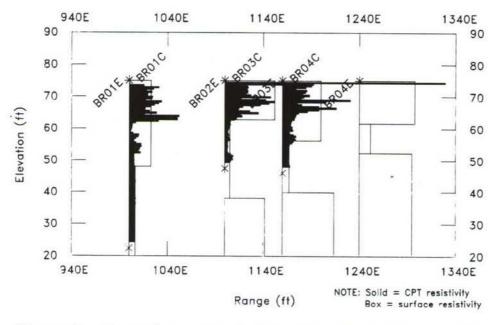


Figure 6. Comparison of Bethel-Royalton Test Site ECPT Resistivity Inversion Profiles.



competent bedrock. Consequently, the resistivity soundings still sense low resistivity ground water as should exist in the fracture zone. This could also explain the presence of a low resistivity zone in sounding inversion BR04E despite not having sensed the water table through pore pressure measurements in penetration BR05C.

It is apparent that surface data or ECPT data alone would have provided ambiguous results for characterizing this site. However, together they provide an expanded synergistic database which provides increased understanding of the site hydrogeologic setting. Figure 7 provides a cross-section of the site showing tip and sleeve data overlaid with an interpretation based on ECPT and surface resistivity results. A complete survey of this site would include seismic reflection surveys to define structure, a full surface resistivity survey to track ground water conductivity levels, and several ECPTs to provide ground truth data.

Homestake Partners Mill Survey

The Homestake Partners uranium mill site near Milan, NM, (Figure 8) provided additional evaluation of the site assessment system. The site has known contamination of salts and heavy metals in a perched aquifer. The contamination source is the mill tailings pile. Ongoing remediation of the site uses pump and treat procedures. Injection wells downstream from the tailings pile near the site boundary pump uncontaminated water from the regional aquifer into the perched aquifer. The intent is to force the contaminated ground water back toward the source where a series of wells extracts the contaminated water for treatment by evaporation.

Figure 9 shows typical ECPT data (penetration HP03C) for the Homestake Partners uranium mill test site. These include electrical resistivity, tip resistance, sleeve resistance, pore pressure, and a shear wave profile. Of particular interest is the zone between the approximately 6540-ft and 6520-ft elevations. This zone is evidenced by low penetration resistance (both tip and sleeve), low electrical resistivity, high pore pressure, and low shear wavespeed; probably a clay zone holding water in capillary suspension.

A cross-section through the site (Figure 10) further illustrates the relation between the shear velocity inversion layer and low tip resistance by including the velocity profile from HPO8C. A second rendering of this section (Figure 11) shows the consistent correlation between high pore pressure and low tip stress. Figure 12 uses ECPT pore pressure and resistivity data to illustrate that the high pore pressure saturated zone is a zone of low resistivity, indicating that resistivity could be a parameter for tracking ground water at this site.

Figure 13 shows a comparison between the logarithm of the ECPT resistivity profile and the logarithm of the profile resulting from inversion of the surface EM data at that location. The agreement in both amplitude and interface depth is very good. This observation suggests that surface resistivity could be correlated with the high pore pressure zones in the soil. Figure 14 illustrates this correlation; low resistivity layers in the inversion profiles agree quite well with the high pore pressure zones, particularly considering the variability in location of these zones and the 3-D nature of the surface measurements.

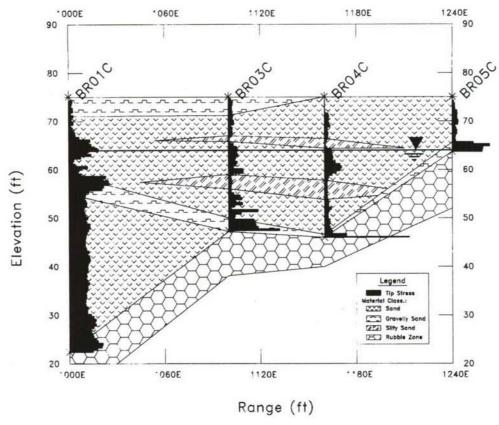


Figure 7. Bethel-Royalton Site Interpretation Based on ECPT and Surface Resistivity Data.

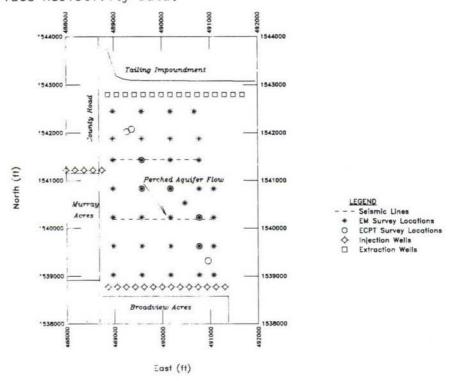




Figure 8. Homestake Partners Test Site Map.

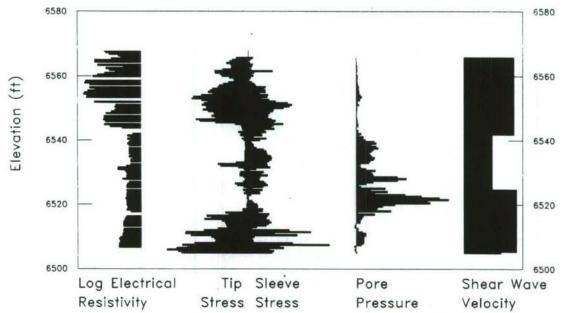


Figure 9. Typical ECPT Data from Homestake Partners Test Site (Penetration HP03C).

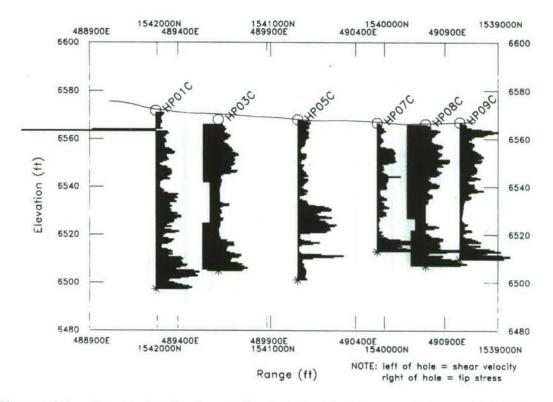


Figure 10. Homestake Partners Test Site Tip Stress Data and Shear Velocity Profiles.



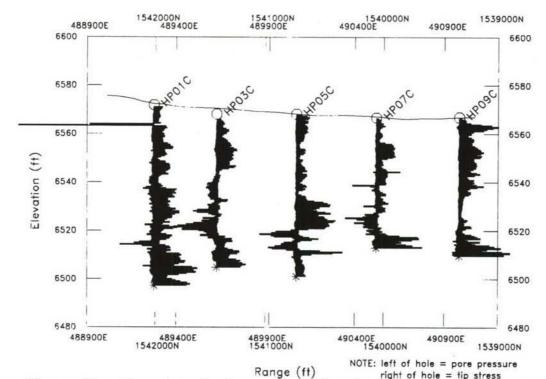


Figure 11. Homestake Partners Test Site Tip Stress and Pore Pressure Data.

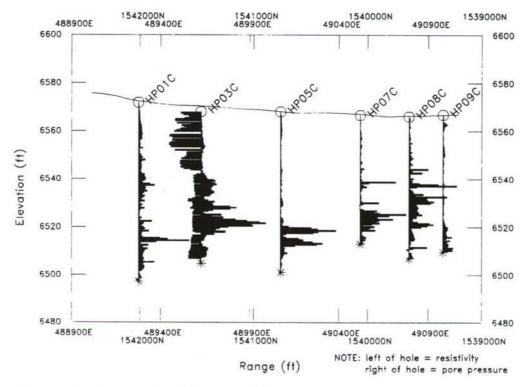




Figure 12. Homestake Partners Test Site Pore Pressure and ECPT Resistivity Data.

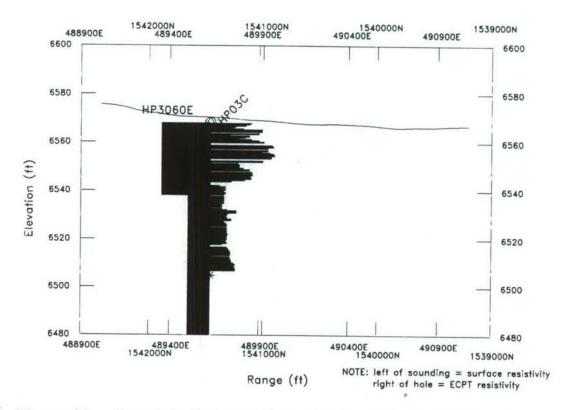


Figure 13. Homestake Partners Test Site Surface Resistivity Inversion Compared to ECPT Resistivity Data.

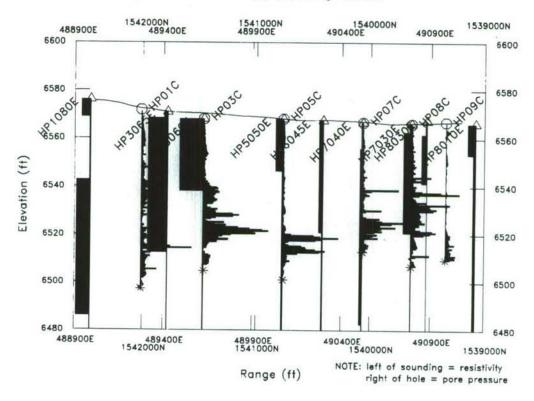


Figure 14. Homestake Partners Test Site Pore Pressure Data and Surface Resistivity Inversion Results.



Data at this site suggest that various ECPT measurements lend insight into a complex hydrogeology. Further, ECPT electric resistivity data provide a direct comparison for the surface resistivity data. A more complete site survey would be expected to provide valuable insight regarding the progress of this site's remediation program.

SUMMARY

Testing at the Bethel-Royalton landfill site demonstrated the synergism between surface and ECPT resistivity. Analysis of surface resistivity measurements, and comparison to ECPT data, demonstrate the ability of the surface technique to provide reliable values for resistivity of subsurface units. However, a major hydrogeologic characteristic of the site, depth to the water table, was misidentified by the surface survey. Direct analysis of the ECPT data provided more reliable information on this variable. On the other hand, the surface survey data provided evidence of the probable extent of the ground water, perhaps in a fractured zone, which was not identified by the penetration tests due to refusal.

Testing at the Homestake Partners Mill site demonstrated the potential for using this system for characterizing a hydrogeologically complex site. Correlation between several physical and geophysical measurements made during penetrometer testing was shown. Correlation was also shown between surface resistivity and penetrometer data.

This study demonstrated the viability of the Minimally Invasive Three-Dimensional Site Characterization System for environmental site assessment. A review of the data achieved using surface geophysics and electric cone penetrometer testing demonstrated that these survey tools can provide complimentary data sets. Combination of these data in a relational database, with a graphical review of the data, resulted in a synergistic effect wherein the combined data revealed characteristics of the sites which would not have otherwise been uncovered.

ACKNOWLEDGEMENT

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SONIC DRILLING FOR ENVIRONMENTAL SAMPLING

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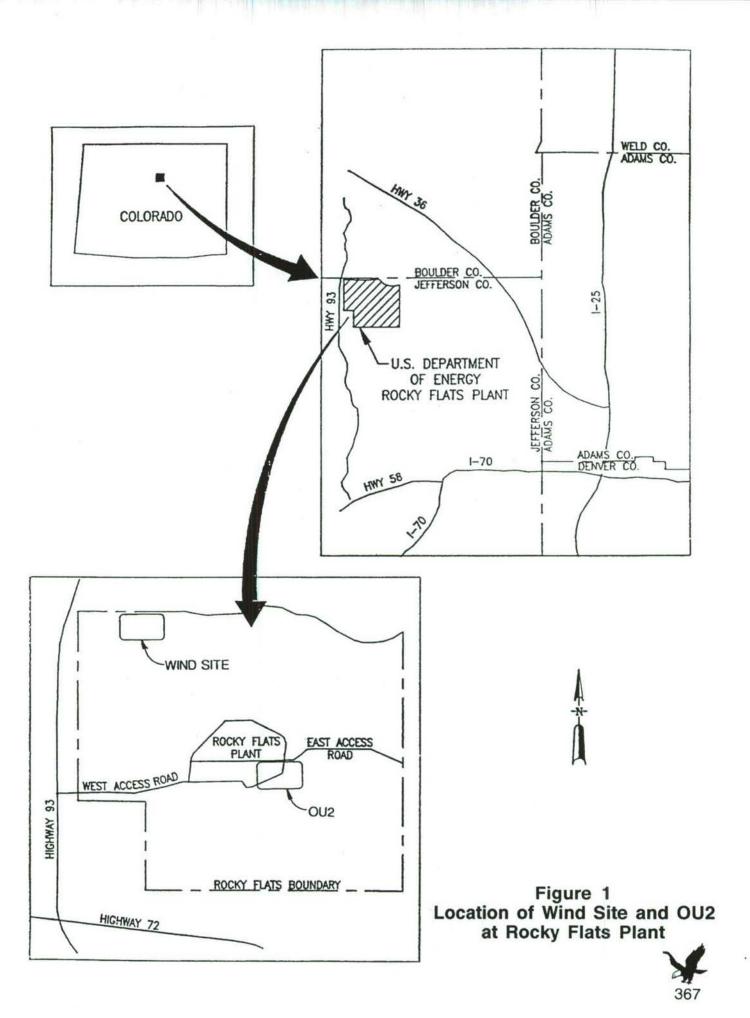
Sonic drilling, a new technology in the environmental industry was used for a subsurface investigation at the Department of Energy's Rocky Flats Facility. This investigation was used to compare the effectiveness of sonic drilling to more conventional hollow-stem auger and air percussion drilling techniques for environmental sampling and monitoring well installation. The hollow-stem auger method has often been the preferred method for drilling and sampling, due to its ability to obtain continuous core and to advance boreholes without the use of drilling fluids. However, hollow-stem augers frequently experience equipment breakdowns when drilling through the large cobbles and boulders associated with the alluvial materials at Rocky Flats. Air percussion drilling allows for the advancement of boreholes through cobbles and boulders, but does not retrieve continuous core samples suitable for chemical analysis and geologic characterization. Air percussion drilling uses air as its drilling "fluid" and generates potentially hazardous dust which usually needs to be contained. Sonic drilling utilizes an oscillating drill head which generates frequencies in the 70-150 Hertz range. This sonic oscillation, combined with slow rotation, advances drill pipe through soil and rock without the use of a drilling fluid. The method was able to obtain continuous core samples similar to hollow-stem augers, including cobbles and boulders. The Sonic drilling and sampling techniques were evaluated for cost effectiveness, borehole advancement rate, temperatures, core recovery, and sample integrity, in similar materials for soil sampling and monitoring well installation. Sonic drilling may have future applications in the environmental industry.

INTRODUCTION

Sonic drilling, a technology developed in the mining industry and recently introduced to the environmental industry, was used for an environmental subsurface investigation of a portion of the Wind Site located in the northwest buffer zone at the Department of Energy's Rocky Flats Facility Plant (RFP) (Figure 1). This investigation was used to compare the effectiveness of sonic drilling to more conventional hollow-stem auger and air percussion drilling techniques for environmental sampling and monitoring well installation. The comparison included information gathered from auger drilling at Operable Unit 2 (OU2) at RFP, where a remedial investigation field program was being conducted at the time of this investigation.

The hollow-stem auger method has often been preferred for drilling and sampling in environmental applications due to its ability to obtain relatively undisturbed samples and to advance boreholes without the use of drilling fluids, which may introduce contaminants to or remove contaminants from the sample and throughout the borehole. However, hollow-stem auger drilling production is frequently slowed by equipment breakdowns when drilling through the large cobbles and boulders associated with the alluvial materials at RFP. Air percussion drilling allows for more rapid advancement of boreholes through cobbles and boulders, but does not retrieve samples suitable for chemical analysis and subsurface geologic characterization. Air percussion drilling uses air as its drilling "fluid" and generates potentially hazardous dust, which usually needs to be contained, resulting in higher drilling costs.

Sonic drilling uses an oscillating drill head that generates frequencies in the 70-150 Hertz range. This sonic oscillation, combined with downward pressure and slow rotation, advances drill pipe through soil and rock without the use of a drilling fluid. The method is able to obtain continuous relatively intact samples similar to those obtained by hollow-stem augers, including cobbles and boulders. The sonic drilling and sampling techniques were compared with hollow stem auger methods in similar materials for cost effectiveness, borehole advancement rate, temperatures, core recovery, and sample integrity, for soil sampling and monitoring well installation. Sonic drilling may have future applications in the environmental industry.



This research project was managed by EG&G Rocky Flats for the Department of Energy. Woodward-Clyde was a technical consultant on the project and Harrison Western corporation was the drilling contractor. The sonic rig and drilling equipment were supplied by Harrison Western, and the sonic equipment modifications for environmental sampling were designed by Snyder Engineering.

The evaluation of the sonic drilling technique is based on data and observations from drilling and installing three wells using the sonic drill in the alluvium at the Wind Site, and two wells using hollow-stem augers in the alluvium at Operable Unit 2 (OU2). The data collected included drilling rates, sample temperatures, and geologic logs of the borings. All of the borings for the wells were drilled into the top of the bedrock underlying the alluvium. The locations of both the Wind Site and OU2 at RFP are shown on Figure 1. The evaluation and comparison are based on drilling in the Rocky Flats Alluvium. The drilling, well installations, and data collection at the two sites were performed by different crews. An indirect comparison with air percussion drilling also was made, based on experience from other locations.

Geology and Hydrology

The surficial deposits at RFP consist of quaternary aged alluvium, colluvium, and valley fill alluvium that unconformably overlay cretaceous aged claystone bedrock. The regional dip of the bedrock is 45-50 degrees to the west, decreasing to approximately 2 degrees to the east in the vicinity of the plant. Groundwater exists under unconfined conditions in the surficial deposits and subcropping sandstones of the upper bedrock formations. Groundwater occurs in confined aquifers in the deeper bedrock.

The Rocky Flats alluvium is a laterally coalescing alluvial fan deposit consisting of poorly to moderately sorted, poorly stratified clays, silts, sands, gravels, and cobbles. The colors of the Rocky Flats alluvium include light to dusky brown, dark yellowish-orange, grayish orange, and dark gray, and forms pediment deposits at RFP. They range in thickness from 0 to 98 feet (Geological Characterization 1991) in the vicinity of RFP and overlay the bedrock formations.



SONIC DRILLING

Sonic drilling uses a relatively high-frequency (70 to 150 Hertz) oscillating drill head combined with downward pressure and slow rotation to advance the drill string through soil and bedrock material. Sonic drilling is accomplished by means of a sonic head located on the drilling derrick. The drill head is vibrationally isolated from the derrick by an airspring. This sonic head produces a frequency close to the natural frequency of the drill pipe, allowing the drill string to act as a flywheel and to transfer the energy of the drill string to the bit in bursts (Figure 2). A small downward force of about 1,000 pounds is applied through the sonic head to the drill string, which is also slowly rotated to aid in presenting fresh material at the bit face. The technique uses a hollow drill pipe with a wireline operated core barrel.

The sonic drill rig used for this project was a trailer-mounted Super Drill SD150 manufactured by Hawker-Sidley and powered by an air-cooled diesel engine. The 160 horse power Deutz turbo diesel engine powers both a 5,000 pounds per square inch (psi) hydraulic pump and a small 100 psi air compressor used for the air spring. The air spring, which is used to isolate the drill head from the mast, uses pressurized air as a spring similar to the way an air shock absorber works. The hydraulic system powers the sonic head, the wireline, winches, leveling jacks, drill advancement, and breakout jaws for the drill pipe. The sonic head usually operates at about 2000 to 2500 psi of hydraulic pressure.

The configuration normally used with sonic drilling is a 7-inch-diameter steel pipe with a carbide studded bit. The bit was designed to direct all of the cuttings toward the center and into the core barrel. This reduces the smearing of clays along the side of the boring. The drill pipe is 6-inch ID with a 7-inch OD at the joints in 5- and 10-foot-long sections. The cuttings are removed using a wireline core barrel. The core barrel is emptied by either tapping on its side or using air pressure above the sample in the barrel to push the sample out of the barrel. This produces a large volume of core/cuttings that can be examined. Significant dilation of the soil structure occurs as a result of the vibration associated with the drilling, and only highly disturbed samples can be taken. The soil does, however, remain in order vertically, allowing discrete sampling of an interval.

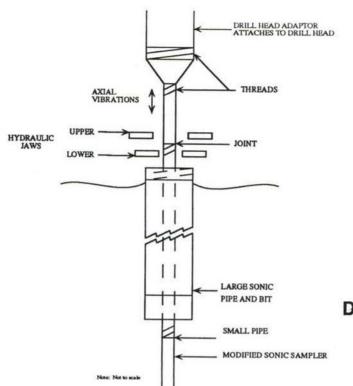
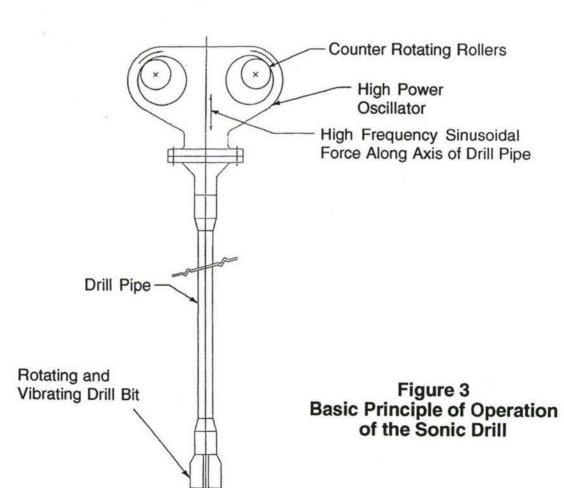


Figure 2
Diagram of Sonic Sampling





SONIC DRILLING FOR ENVIRONMENTAL SAMPLING

The sonic drilling method was modified prior to the investigation at the Wind Site so that soil samples from the sonic drilling would be similar to the samples obtained with continuous sampling auger drilling techniques at RFP. This was done by down sizing and modifying the sample barrel from 5 inch ID to 2.5 inch ID. This included the design and manufacture of a new sampler that produces a sample the same size (2.5 inch) as the continuous sample from an auger rig, and associated drill pipe and adapters. The modified sonic equipment was designed to fit through the sonic bit with the 7-inch-diameter (large sonic) drill pipe in place (Figure 3).

The modified sampler bit was designed so that the cuttings would be pushed to the outside of the bit as it was advanced and a relatively undisturbed sample would be obtained. The cuttings would then be included in the cuttings/core from the larger sonic drill pipe. The bit on the large sonic pipe is designed so that the cuttings are directed into the center of the drill pipe.

Sampling with the modified 2.5-inch-ID sonic sampler involved sampling through the 5-inch-ID drill pipe. The sampler was advanced 5 feet, in two 2.5-foot runs. The sampler was removed from the boring between runs. The 5-inch-ID drill pipe was the advanced to the bottom of the second sample and the process repeated. Figure 3 shows the modified sonic equipment in place, sampling through the large sonic drill pipe and bit.

Field Modifications

The bit on the modified sampler was modified in the field after the first hole to eliminate the flanges on the bit, which were meant to aid in moving soil to the side during drilling and to limit the amount of cuttings that would end up in the sample. The elimination of the flanges reduced the disturbance of the surrounding soils during advancement. This modification was successful in that the disturbance of the surrounding soils was reduced, as was the necessary downward force to advance the sampler. After the field modification, the sampler was able to make three consecutive 2-foot runs with the boring remaining open to a depth of 6 feet below the large sonic drill bit without caving.

The consecutive 2-foot runs with the field modified sampler required the removal of all the small drill pipe and reinsertion for each run. Each trip in and out of the boring required the pipe section joints to be broken loose with the rig's hydraulic jaws. After the field modified sampler had advanced 5 feet, the large sonic drill was then able to advance 5 feet, and the sampling with the field modified sampler was continued from that point. The downward force used to advance the field modified sampler was reduced to less than that necessary to advance the large drill pipe.

Both the original sampler and the field modified sampler encountered problems making 2-foot runs in the cobbly materials. This was due to the cobbly material fragmenting to a rock flour texture and plugging the bit both before and after the field modification.

Well Installation

Well construction with sonic equipment is similar to well construction with hollow stem auger and air percussion. Once the well casing is in place, bentonite pellets are placed around the sump, below the well screen. The drill pipe is then pulled up from the bottom of the boring. The filter pack is added as described above. The vibration of the sonic drill pipe as it is being pulled prevents the sand from bridging between it and the well casing and also compacts the sand/gravel filter pack around the well casing. Above the sand, the well construction through the sonic drill pipe and hollow stem augers is the same.

Drilling

Drilling times, boring and well depths, well construction time, mechanical down time and well construction rates are summarized in Table 1.

The three sonic borings and well installations at the Wind Site took about a week each to complete. The drilling was slowed due to problems with the sampler becoming clogged by fragmented cobbles or gravel during sampling runs. As a result, some of the samples were obtained using a stainless steel scoop to take the sample from the large sonic core barrel. This was done when drilling with the modified sampler was not deemed feasible due to probable plugging with cobbles or gravel. During drilling of the



TABLE 1
DRILLING TIME AND RATE SUMMARY

Site	OU2	OU2	WS ¹	WS	WS
Well Number	07291	09091	45091	45191	45291
Boring Depth (ft)	26.5	29.6	42.3	51.2	43.3
Well Depth (ft)	22.6	26.7	42.3	49.4	41.8
Total Drilling Time (hrs) ²	6	8	10	15.5	12.25
Well Construction Time (hrs)	1.75	3	8.5	16	6
Rig Down Time (hrs) ³	0	4	0.5	1	1.75
Well Construction Rate (hrs/ft) ⁴	0.34	0.56	0.45	0.66	0.48
Well Cost (\$/ft) ^{5,6}	36	59	116	170	123

Notes 1. WS - Wind Site

2. Total Drilling Time includes auger pulling and reaming time for hollow stem augers.

3. Rig Down Time for mechanical problems only.

4. Well Construction Rate = well drilling + well construction + rig down well depth

- 5. Well cost does not include materials, only drillers cost.
- 6. Auger rig at \$105/hr, sonic rig at \$257/hr.

second boring with the modified sonic sampler, the drill head adaptor for the small pipe snapped at the to of the threaded section. The drill head adaptor for the small pipe was later inverted to again allow use of the sampler and small pipe. Problems were also encountered during the well construction due to the vibration-induced liquefaction of the grout around the sump during placement of the sand filter. The well was cleaned out by redrilling and reconstructed. The well casing floated during sand placement while the drill pipe was being vibrated in place.

The two hollow stem auger borings and well installation at OU2 took about three days each. During drilling of one of the borings an automatic shutdown switch on the rig failed and prevented the rig from being started. The switch was replaced, and the well drilling and construction completed.

SUBSURFACE CONDITIONS

Wind Site Subsurface Conditions

The three sonic well borings 45091, 45191, and 45291 were advanced through the alluvium and into bedrock. The alluvium encountered during the investigation generally consisted of fining upward outwash sequences with cobbly gravels at the base and silts and clays at the top. The gravels throughout the borings are predominantly quartzite with granite fragments, and traces of schists and gneiss. Arkosic arenite gravels and cobbles found below 20 feet and increased in content and size with depth to bedrock.

OU2 Site Subsurface Conditions

The two auger well borings 07291 and 09091 went through the alluvium and into bedrock. The alluvium encountered during the investigation primarily consisted of sandy gravel with clay and some silty lenses. The gravels throughout the borings are predominantly quartzite with granite fragments, and trace schists and gneiss. The bedrock in both borings were claystones with some silty and sandy zones of the Arapahoe Formation, a typically weakly cemented sedimentary formation.



OTHER FIELD DATA AND OBSERVATIONS

This section describes problems that were encountered with the sonic sampling equipment. First noted was the amount of wear on the carbide inserts in the modified sampler bit after the first few runs. The carbide inserts had been rounded off and other signs of wear on the inserts and bit steel were readily visible.

Stress on the small drill pipe was observed in the wear of the plating on the threads. The plating was wearing off within the first few runs even though corn oil was applied as a lubricant. The stress in the threaded section of the drill head adaptor for the small drill pipe was made apparent by its failure midway through the second boring. The hydraulic lines on the rig also experienced some vibrational stress causing one of the metal pipe lines to fracture and leak during drilling of the first boring. This was readily fixed by replacement of the section with a flexible line.

The modified sampler experienced trouble during its first few runs, including caving of the hole after the sampler was removed; bit clogging as a result of fragmenting of cobble to rock flour; and scorching or drying of the exterior of the samples in the sampler. This forced the section to be redrilled through the caved material to sample the next interval. The modified sampler was only able to advance 0.5 to 1.5 feet in the cobbly materials before refusal was reached. A downward force, which was higher than the design specifications and higher than that used to advance the large sonic drill pipe, was required to advance the modified sampler. The modified sampler pipe sections could only be separated using the rig's hydraulic jaws because the energy transmitted through the pipe caused the joints to tighten. Because the hydraulic jaws were required to break loose the pipe joints of the modified sonic sampler, this meant that 5 or 10 feet of sampling needed to be completed between advances of the large sampler. The soil samples from the modified sampler and large sonic core barrel also had problems with color and moisture changes due to heat. The vertical positions of the materials in the sampler were not accurate and features like fractures and bedding were obliterated. However, the large sonic drill bit and core barrel were able to core through the sides of cobbles and obtain pieces.

DRILLING METHOD EVALUATION

Since sonic drilling has only recently been applied to environmental investigations, objective evaluation criteria for this technique were developed. The drilling method evaluation is divided into two parts. A quantitative evaluation is discussed first and includes a drilling rate comparison with auger rigs operating at RFP on the OU2 project in similar geologic conditions. Based on this drilling rate comparison, a cost comparison of the two techniques is also included. Included in the cost for both types of rigs is a percent downtime for equipment repairs and other associated costs. The second part, a qualitative evaluation, includes the other measurements that were made for comparison purposes, including visual disturbance, and chemical data quality for sonic, auger and air percussion rigs.

Quantitative Evaluation

The quantitative evaluation includes information measured at Rocky Flats for both the sonic rig and for an auger rig. Values for the air percussion rig are based on experience at other locations with similar geology and are not directly comparable. Table 2 is a summary of the quantitative evaluation.

The total drilling and well construction times are summarized in Table 1. The drilling rates for the sonic rig were generally slower when the small pipe and the modified sampler were being used. The trip times for the modified sonic sampler were generally about 30 minutes, including changing the core barrel, and are longer than comparable trip times with an auger, which are about 10 minutes. This is because the joints between the pipe sections have to be threaded and unthreaded every trip in and out of the boring. The time and effort required for this threading and unthreading of the pipe depended on how tight the threads had become during drilling. The drilling rate for the large sonic sampler is also slower because more runs are needed to go the same depth as an auger.

The well construction times with the sonic rig were also longer, mainly due to crew inexperience. It should be noted that the well construction time was cut from 8.5 to 6 hours between the first and third wells, and further improvements in well construction

TABLE 2
SONIC, HOLLOW STEM AUGER AND AIR PERCUSSION
QUANTITATIVE COMPARISON

Drilling Method	Sonic	Hollow Stem Auger	Air Percussion
Drilling rate (ft/hr)	3-5	3-5	8-10
Well Cost (\$/ft)	135	50	NM¹
Soil Temperature (°F)	50-135	50-90	NM
Soil Recovery ²	100-200	30-50	0%

Notes

- 1. NM Not Measured
- 2. Sample recovery in alluvial material on a length basis.

time could be expected with increased experience with the sonic equipment. Drilling and well construction times for hollow-stem augers and sonic drilling are shown on Table 1. Average drilling rates for hollow-stem auger, sonic, and air percussion drilling are summarized in Table 2 and are based on experience at this and other sites with similar materials.

Auger rigs in the Denver area currently cost about \$100 to \$120 per hour, with standby rates of about \$15 per hour lower. Air percussion rigs cost about \$250 per hour, with standby rates of about \$220 per hour. The sonic rig costs \$257 per hour, with a standby rate of \$221 per hour. All of the rates will vary depending on the job and location. Typically, for local jobs, mobilization is billed on an hourly basis and/or a milage basis.

The cost of well installation on a per-foot basis with the sonic rig (\$135 /ft) was about 2.5 times that of an auger rig (\$50 /ft) based on the five wells drilled for this study. The reasons for the higher cost with a sonic rig are twofold: (1) the drilling and well

construction is currently slower, and (2) the hourly costs for a sonic rig are over two times the auger costs.

The soil temperatures measured in the auger samplers ranged from 56 to 92 degrees Fahrenheit (F) in the soil above the water table. Once the water table was reached, the soil temperatures dropped to the low 50s, which is probably the ambient soil and groundwater temperature. The temperatures for the soils from the large sonic sampler varied from 50 to 136 F degrees and for the modified sonic sampler varied from 50 to 122 degrees F in the dry materials. The temperatures for the sonic samplers also dropped to the 50s and low 60s once the water table was reached. The temperatures tended to increase with increased drilling time (min/ft), and drilling time generally increased with increasing grain size. When the moisture content of the soil increased, generally the soil temperatures decreased. A few measurements of the modified sonic sampler's bit temperature were taken, and they ranged from 140 to over 220 degrees F (the upper limit of the thermometer).

The sample recovery rates (length of sample/length drilled) for the sonic varied from 0 to 411 percent depending on the material that was being drilled and the size of the pipe. Generally, the large pipe had recoveries of 100 to 200 percent of the drilled length or 50 to 100 percent on a volume basis. The high recovery rates of up to 200 percent are not unexpected for the large sonic because the area cut by the bit is twice the area of the core barrel; and the volume cut is about equal to the volume recovered. The modified sonic sampler had recoveries of 80 to 180 percent in the finer grained materials and 20 to 40 percent in the coarser grained materials, due in large part to the larger materials becoming fragmented during drilling and clogging the bit.

The sample recovery rate was measured in two borings drilled at OU2. The sample recovery rate of the hollow-stem auger continuous coring technique varied from 0 to 65 percent in the alluvium and from 0 to 100 percent in the bedrock. The average recovery in the alluvium was 38 percent. The bedrock recovery is hard to quantify because in one boring the recoveries were all 100 percent and in the other from 0 to 5 percent.

Air percussion recovery rates were not measured as part of this project. Normally recovery of samples usable for detailed logging or analytical chemistry testing is not



possible because the drilling method does not produce any core. Air percussion drilling generally produces sand size fragments, sand, and dust as it advances the boring. Sampling is possible with drive or push samplers using standard equipment.

The modified sampler took about twice as much downward pressure to advance as the larger pipe, prior to the field modification. This is probably due to its much larger area ratio (area of bit or sampler to area of sample) before the field modification. After the field modification was made, the downward pressures for the field modified sampler were lower than those for the large sonic.

Carbide wear on the modified sonic bit was dramatic during the first two runs, especially on the outer carbide inserts on the drill bit flanges. The smaller pipe had high stresses as evidenced by its failure during drilling of the second boring. This failure occurred after only about 20 feet of drilling with the modified sampler and small pipe. The high stress was also visible in the wear of the plating on the threads of some of the small pipe.

The field modification of the sampler reduced hole caving when withdrawn from the boring. Before the field modification, the boring would collapse after the modified sampler was withdrawn, and only about 0.5 feet would be open after a 2-foot run. Once the field modification was made, and after the field modified sampler was withdrawn, the borings were able to remain open to a depth of 6 feet below the bottom of the large sonic bit. This was due in large part to the decrease in disturbance of the ground around the field modified sampler and the lateral compaction of the soils. The lateral compaction of the soils was caused by the cuttings being forced to the outside due to the bit design. These cuttings were then removed by the large sonic as it was advanced.

Qualitative Evaluation

This section deals with the less easily quantifiable parts of the evaluation. Table 3 summarizes the qualitative factors for sonic, hollow-stem auger, and air percussion drilling. The factors include sample disturbance, lithology, chemical data quality, vertical spread of contaminants, drilling fluid, decontamination, noise levels, boring alignment, and well construction and condition.

TABLE 3

SONIC, HOLLOW-STEM AUGERS AND AIR PERCUSSION DRILLING COMPARISON

0	So	Sonic	Hollow-Stem Auger	Air Percussion
	Large (5.1" ID)	Small (2.4" ID)		
Sample Disturbance	Very Dist.	Moderate	low	needs secondary method - i.e. splitspoon
Lithology	exact locations not possible but within a few tenths of a foot, large volume, no bedding features	t possible but is of a foot, large ng features	good where samples are recovered	misses thin layers-gravel is pulverized difficult to log accurately
Chemical data quality	VOA's questional dilation and heat	VOA's questionable due to sample dilation and heat	good quality	depends on sampling method
Vertical spread of contaminants	minimal vertical smearing	mearing	vertical smearing high	minimal vertical smearing
Decontamination	easy		difficult	easy
Drilling fluid	none		none	air needs to be filtered, dust into bag
Noise level	low to moderate (may desire hearing protection)	may desire	moderate (hearing protection advised)	high (hearing protection normally required)
Boring alignment	straight		subject to deviation	slightly subject to deviation
Well construction	average to good		average	average to difficult
Well condition	good to excellent		boog	good to poor
Depth limit	700 ft max. to date normal 300 ft up to 10 in. diam.	e normal diam.	good to approx. 100-150 ft	300 ft or more depending on rig

There are some differences between the large and the small samples obtained from sonic drilling. The small samples appeared less disturbed. Some bedding and fracturing could be seen in the sample; however, it was not as easily visible as it was in continuous sample from an auger. The outside edges of the 2.5-inch samples were visually dried out during the sampling process. The large samples tended to produce large volumes of material to test. However, the larger sample was, generally, very disturbed to the extent that no bedding was observable, and only gradual changes in materials were visible. This included fining upward sequences and major changes in lithology. The high disturbance of the samples, however, does not preclude the ability of the method to obtain discrete samples from a specified interval. Generally, for environmental sampling, the sample disturbance is not important, but the discreetness of the sample is. However, relatively undisturbed samples allow for better geologic descriptions and a better understanding of the subsurface hydrogeologic conditions, which are important to the understanding of the nature and extent of the contaminants.

Chemical data quality from hollow-stem auger sampling is the current industry standard and generally produces good quality. When very stiff dry cohesive or very dense dry granular soils are encountered using the sonic equipment, the soil temperatures in the sampler were elevated. The elevated temperatures, the loosening, and the expansion of the soils during sampling with the sonic equipment may have decreased the levels of volatile and semivolatile compounds in the samples. Most other chemical data should be of good quality because they are not affected by temperature or disturbance of the soil. Chemical data quality for air percussion sampling would depend on the sampling method used.

The down sizing of the sonic equipment was not effective. This resulted in numerous problems with the modified sampler and the small sonic equipment. The primary problem was that the threads on the pipe could not take the high cyclic or repetitive stress resulting from the vibrational nature of the drilling equipment. In addition to the adaptor to the vibratory head breaking, the threads on the small drill pipe experienced wear due to the stress. A standard API or similar pipe may have been more cost effective in down sizing the pipe and better able to handle the stresses. The down sizing also increased the soil temperatures. The soil temperature increase was probably due to the high frictional heat generated by the vibration and slower rate of advancement.

The vertical spread of contamination by drilling is limited to the area disturbed during drilling. This is generally minor and usually occurs by cuttings being smeared up the sides of a boring by the augers. This upward smearing of soil does not occur with either sonic or air percussion drilling because the cuttings are typically brought out through the drill pipe or casing. The smooth wall of the pipe/casing used in sonic and air percussion also lend themselves to easy, rapid decontamination compared with hollow-stem augers, which tend to collect soil on the auger flights.

Air percussion drilling uses high velocity air as the fluid to remove the cuttings from the bit. This air flow is generally cycloned to remove the large particles, and the dust is released to the atmosphere. However, for drilling in hazardous areas, the air may need to flow through a particulate and volatiles capture system, which would increase costs. The noise from high velocity air, combined with the percussion noise from advancing the drill casing, normally makes hearing protection required for air percussion drill rigs. Hollow-stem auger rigs drilling in difficult conditions also tend to make high decibel levels of noise which makes hearing protection advisable. The noise levels from the sonic rig are low enough that hearing protection is not required; however, as with most large equipment, it is desirable.

Borings with sonic and air percussion rigs are usually straight and are not typically subject to deviation, but will instead core through hard objects like cobbles or pipe. Augers are subject to deviation, being knocked out of vertical by hard objects due to their rotary advancement. A hard object may be forced to the side or force the auger to the side. This lateral deflection of the boring is usually not critical, but does increase the stress on the augers and other equipment.

Well construction with hollow-stem augers is generally easy but can be difficult in poor conditions, such as flowing sands. Well construction with sonic is also generally easy, but the well casing tends to float upward during sand placement. This floating of the well casing was probably caused by the sand and bentonite pellets being liquified by the vibration of drill pipe. This problem would probably be reduced with increased experience in well construction with the sonic equipment. Well construction with air percussion equipment is difficult in part because of the difficulty in drill casing removal.



The condition of the well after construction is related to the difficulty in well construction and also the condition of the filter pack. The gravel (sand) filter pack material for both hollow-stem augers and air percussion is normally placed by free fall or through a tremie and is not compacted or densified. This method of placing sand can cause bridging of the sand between the augers or casing and the well casing. These sand bridges are capable of lifting the well casing. Another problem can occur when the auger is lifted too rapidly, and soil caves into the filter sand. A sonic rig vibrates the gravel (sand) filter pack material during placement, which should result in a denser, more effective filter pack free of voids and soil inclusions. The vibrations also prevent the sand from bridging between the drill pipe and the well casing.

Auger drilling is commonly used to depths of 100 to 150 feet, depending on the materials being drilled. Air percussion equipment is generally used to depths of about 300 feet or more. Both auger and air percussion rigs are limited in depth by their rig sizes and available torque. Sonic equipment is normally used to depths of 300 feet but has been used to depths of 700 feet, with typical pipe diameters of up to 10 inches auger.

CONCLUSIONS

The sonic drilling worked favorably in the alluvium. The sonic rig's drilling rates were slower than the auger rig's drilling rates for similar conditions within the alluvium. With a well construction cost of \$135 /ft, it was not cost effective compared to hollow-stem auger well construction at \$50 /ft for the sites included in this study. Sonic drilling may, however, be more effective in bedrock or other difficult drilling conditions because its drilling rate remains relatively constant with differing material and depths, whereas augers tend to slow with increasing depth and hardness. The air percussion drilling also is better in bedrock than augers; however, no analyzable sample is usually recovered without separate sampling equipment.

Sonic drilling and sampling is acceptable for discrete disturbed sampling of soils, but may produce questionable samples for chemical analysis due to relatively high temperatures created during drilling and sampling. The rate of core recovery for sonic sampling at 50 to 100 percent by volume and 100 to 200 percent by length is better than the auger recovery rate of 30 to 50 percent by length in the alluvium. The samples produced by

the sonic equipment are more difficult to log due to its disturbance of bedding, fracturing, and other small features compared with samples from hollow-stem augers. The comparison of sonic equipment with both hollow stem augers and air percussion equipment is summarized in Tables 2 and 3.

Sonic drilling appears to have excellent potential in specific applications. These applications include locations where large boulders or fractured crystalline bedrock like basalt or granite need to be sampled or wells installed. The equipment needs further improvements and testing to address concerns about high temperatures and costs before it will be widely used and accepted in the environmental field.

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DESIGN AND OPERATION OF WELL FIELDS AT HAZARDOUS WASTE SITES: A CASE STUDY

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Abstract

Wastes from chemical manufacture have been dumped in sludge lagoons at Muskegon, MI for many years. The seepage, which contains benzidine, dichlorobenzidine, methyl chloride, benzene, aniline and azobenzene, among many other less toxic materials, has contaminated the groundwater and threatens a nearby creek. The compounds mentioned are either potential or known human carcinogens. Contamination is sufficiently elevated for the local risk factor to be extremely high and has caused the area to be placed on the National Priorities List as a "Superfund Site." To prevent migration of the contaminated groundwater, a series of collection wells were installed for continuous operation to prevent migration of the contaminated plume. There are minimal records concerning their installation, operation or maintenance. When the U.S. Army Corps of Engineers (CE) and the Environmental Protection Agency (EPA) became involved in the management of this site, it was evident that the wells were plugging to the extent that their continued operation was unlikely. Loss of capture of the contaminated groundwater plume could threaten local aquatic resources including Lake Michigan. Previous attempts to overcome severe well incrustation have been restricted to perfunctory cleaning efforts and the installation of new wells. is exacerbated by the corrosive failure of piping and pumps in the water extraction system in as little time as six months, in spite of the fact that the water is not classically aggressive

(i.e., not of extreme pH or high salt concentration). Through research conducted by the CE involving Alford, Rogers, Cullimore Concepts Inc. (ARCC) the problem was identified as a microbial one. ARCC cleaned the wells in September 1991 by a process in which heat and various chemical agents are applied. This and the preventive maintenance program for the well field will be described. These efforts will allow the wells to continue in operation until a new system can be designed and installed. Details of this, which will facilitate monitoring and maintenance, will be presented. Examination of the biofouling material (biofilm) in the wells revealed yet a further problem. The biofilm was found to concentrate the pollutants at least 10 fold over the levels in the groundwater. The fouling of wells with so-called iron bacteria and subsequent precipitation of ochre is familiar to those who manage water systems. Here the "collection well" solution becomes the problem because the wells must now be considered as point sources of carcinogenic contamination. This poses serious problems in their cleaning, abandonment and removal. In contrast to the water handled by wells used to relieve hydraulic pressures associated with dams, etc., that in "pump and treat" efforts often contains high levels of those nutrients that limit bacterial growth in pristine environments (nitrogen and phosphorus). We can be certain that in these circumstances microbial fouling will occur - it is only the kinetics and extent that will be in doubt!

INTRODUCTION

Groundwater that has been polluted by man's above-ground activities is usually brought to the surface for reclamation. After treatment, it is often re-injected or discharged to surface to drain away. Both of these procedures require the use of wells, infiltration galleries or discharge piping, and are usually referred to collectively as a pump and treat operation. It is well known among the environmental microbiology community that whenever water flows over a surface, that surface becomes covered with a film of microorganisms, usually called a biofilm. Thus, a biofilm is a concentration of microbial cells and their products at an interface. In an extraction and reinjection system for the remediation of groundwater, the entire system is at risk of being colonized by microbes. Even layers of cells a few tens of micrometers thick can cause considerable hydrodynamic drag. However, in many cases, the biofilm becomes anaerobic at the metal-biofilm interface because the removal of oxygen by the microorganisms is faster than its diffusion rate in the film. This in turn sets the scene for the onset of microbially-enhanced corrosion. Such biodeterioration can bring a plant to a complete standstill in a matter of weeks. Probably the most infamous example of this is the total shut down of the \$0.5 billion Synfuels plant in the Mid-West that closed because of biofouling problems six weeks after coming on line. Fouling problems are found in <u>all</u> wells, even those used to pump drinking water where the levels of nutrients for microbial growth are often very low. In relief wells on dams, the problems are somewhat greater, especially where the iron content of the water is above 0.2mg $\rm L^{-1}$. In extraction wells involved in groundwater remediation, the water may contain (at significant levels) many of the nutrients that normally limit microbial growth as well as sources of carbon The limiting nutrients are usually nitrogen and and energy. phosphorus. These can arise as breakdown products of compounds such as amines and organic phosphates used in dye and pesticide manufacture. Under conditions where microbial growth requirements are satisfied, there will be comparatively rapid

microbial reproduction.

We will describe an area that has been placed on the national priorities list as a Superfund Site' where the problems mentioned are found at serious levels. Because of the highly toxic nature of the chemicals found in the groundwater at this location, the situation is further exacerbated and complicates our attempts to remediate the groundwater and maintain the physical plant. Although they are not always recognized as such, we believe the problems we will describe are the norm rather than the exception.

DESCRIPTION OF THE AREA.

The site, which is 85 acres, is located in Muskegon County, MI, six miles east from the town of Muskegon (Figure 1). It slopes gently from the North to the Southern-most boundary except near Big Black Creek where slopes may be as much as 30% on some lagoon berms adjacent to the floodplain. Big Black Creek, which is close to the Southern boundary, is currently being used for recreational activities. Either side of the creek are areas of designated wetlands.

The overburden in the area consists of Quaternary sediments of Recent and Pleistocene age (Figure 2). The Recent sediments are alluvial deposits associated with Big Black Creek, and consist of reworked glacial sands and overbank deposits of silt, clay and organic matter. The Pleistocene sediments consist of glacio-lacustrine fine to medium sands with variable amounts of fines. This sand unit is approximately 80 to 115 feet thick across the site area. Approximately two-thirds of the sand unit is saturated. Underlying the sand unit is a glacial till, approximately 140 feet thick, which act as a confining layer to the underlying Mississippian age Marshall Sandstone. The glacial till is comprised of predominantly silty clay. The Marshall Sandstone could be used as a drinking water aquifer, but since it is high in iron and other dissolved solids, it is of limited use in the Muskegon area.

The geology of the area, i.e. highly permeable sands and silts, dictates that there will be little or no run-off. The



majority of precipitation infiltrates rapidly and transports ground-associated substances downwards. The majority of wells are completed in the glacial sediments as they provide relatively shallow drilling depths, good porosity and permeability, and good water quality. Thus the area of most concern is the sandy unit. THE CONTAMINATION PROBLEM.

Lakeway Chemicals began producing industrial chemicals at the site in 1960. Throughout the 1960's and early 1970's, ten on-site unlined catchment and storage lagoons were used for disposal of sludge, wastewater and various waste liquids. Apart from the current manufacturing company, the Bofors-Nobel Company were the most recent operators of the plant and were the operating company when the site was placed on the National Priorities list by the U.S. Environmental Protection Agency in March, 1989. The fact that several companies have operated the plant at this location has lead to a paucity of historical information concerning the nature of the materials dumped in the lagoons. As mentioned earlier, because of the geological nature of the area, chemical compounds deposited in the lagoons have contaminated the saturated soils and sediments underlying the area. The area poses a principle threat to human health and the environment because of the risks associated with contaminant migration from the sludges and soils into the sandy aquifer directly under the site. If the contaminated groundwater in these aquifers discharges directly into Big Black Creek, it also will pose a risk from ingestion of creek water since this is a swimming area. There is further a threat from inhalation of volatile contaminants directly from the sludges and soils.

In the lagoon area, ten potential source areas were identified, i.e. areas associated with the ten settlement lagoons and the lagoons themselves. As could be expected, the magnitude of the contamination varies considerably among the source areas. The compounds that are responsible for considering this site potentially dangerous to human health are: methylene chloride, 3, 31-dichlorobenzidine, aniline, azobenzene, benzene and benzidine. All are highly toxic. The first four are potentially

carcinogenic in humans; the last two are known human carcinogens. Although the sludges contain considerable quantities of metals, these were not considered to be compounds of concern here because of their lack of leachability from the sludge (pH>8). Approximately 0.5x10⁶ yd³ of total contaminated soils is estimated to be at this site.

INITIAL ATTEMPTS AT CONTAINMENT.

The immediate environmental health concern is migration of contaminated water from the location. In the 1970's the State of Michigan placed various restrictions on wastewater disposal from the site. In 1976 purge wells were installed to extract contaminated groundwater and provide hydraulic containment for the contaminated plume. The system maintained by the State consists of 12 primary and back-up wells constructed along the southern portion of the property, i.e. to prevent contaminated water from leaving the site boundaries. Unfortunately, documentation with regard to the drilling and installation of these purge wells is now lacking, as is also the case for the performance and maintenance information. Early on it was found that the purge wells were very susceptible to encrustation' with concomitant loss of efficiency. Solutions to this problem included treatment of the wells with acid (which proved ineffective) or even their total replacement. In spite of the logistical problems in operating this well field it is, under ideal circumstances, capable of preventing the migration of the contaminated groundwater plume. Currently, approximately one million gallons of groundwater per day is pumped to a treatment system which in turn discharges to the Muskegon County wastewater treatment plant. Dissolution and leaching of compounds from the sludge and soil appear to be the primary transport mechanism to the groundwater in the upper sandy aquifer. Based on historical data and groundwater modeling, if the pumping system is turned off or becomes non-functional, the contaminated water will discharge into Big Black Creek.

SPECIFIC PROBLEMS ENCOUNTERED.

Plugging of wells and piping with microbial growth is a



problem that is easily detected through flow measurements, however another major concern that is not so easily detected is corrosion (Figures 3&4). Pumps sometimes last less than six months before they need to be replaced. This is in a situation where the pumped liquid is not aggressively corrosive. Its pH is about 8.0 and it does not contain high concentrations of The problem is one of microbially-enhanced corrosive salts. corrosion (MEC). Samples of the material plugging the wells in corroded areas is found to contain high levels of iron and sulfide (Figure 5). These are typical end-products of the metabolism of sulfate reducing bacteria (SRB). MEC is found where oxygen is limiting aerobic microbial growth. In other words there is more organic material available as a source of microbial nutrition than there is oxygen to process it aerobically. The problems at this site are further complicated by the fact that much of the material placed in the lagoons are detergents or compounds related to their manufacture. causes foaming problems wherever water is moved at pumping velocities.

CHEMICAL AND TOXICOLOGICAL CONSIDERATIONS.

As mentioned earlier, the chemical composition of soils and sludges varies with each lagoon. It is also the case that the purge well discharge water varies too. Rather than indulge in an encyclopedic description of the 12 purge wells and their effluent analysis, we will focus on one of them that is particularly prone to deterioration. The most toxic of the compounds found at the B-N location is benzidine. Its levels in the purge well effluent of a selected well varied during five years from a low of 0.7mg L¹ in 1989 to a high of 16.6mg L⁻¹ in February 1991. concentration of $1\mu g \ L^{-1}$ is considered carcinogenic. There is little point in undertaking trend analysis of the data collected from 1987 to 1991 since there are no records of the materials dumped in the lagoons, well performance, or cleaning operations during this time. In February 1991, for the first time, analyses of sludge scraped from the inside of the well were compared to the analysis of the discharge water. Similar sludge was sampled

and reanalyzed in September 1991. Table 1 shows that in February, the solid material encrusting the well was 25 times higher in benzidine than the water.

TABLE 1
SOME ANALYSES OF BENZIDINE FROM PURGE WELL 34

DATE	AQUEOUS	SLUDGE (Biomass)
	$mg L^{-1}$	mg Kg-1
FEB 91	16.6	417
SEP 91		8.087

By September the level in the sludge had risen to over 8,000 mg/Kg. The biomass, the products of its metabolism and accretions have concentrated the toxic material many fold. Unfortunately, we do not have enough samples at this time to carry out statistical analysis of the results. This is planned at the next sampling time in June, 1992.

PROPOSAL FOR INCREASED RELIABILITY.

New extraction wells (15) will be installed to replace the corroded existing wells. Although they will not be increased in diameter (8"), a preventive maintenance program will be initiated. The construction material will be stainless (type 304) or standard steel for the casing, but the well screens all will be of stainless steel. The preventive maintenance program will be based on that developed by Alford, Rogers, Cullimore Concepts, Inc. (ARCC) in conjunction with the Army Corps of Engineers. The process is unique in that heat and various chemical agents are applied to the well. The process has had great success in remediation of several types of wells. It was applied as a cleaning process aimed at well recovery (rather than maintenance) to the worst effected wells on the B-N site in September 1991. Its success at that time should allow the operation of the extraction well field until the new purge wells can be installed. In order to prevent cross microbial contamination of wells, all equipment will be sanitized with steam and sodium hypochlorite solution before being placed in a

well. The wells themselves will also be treated with hypochlorite solution to lower their microbial content before being placed in service. In addition to the preventive maintenance program, well performance and the results of microbiological testing will be recorded at intervals of three months. A further innovation may be the drilling of satellite injection wells around the extraction well. Cleaning chemicals could be pumped to the well environment without taking it out of service. The extraction pump would serve to cause these chemicals to flow towards the main well, hopefully removing biofouling material in the aquifer at the same time. These added injection wells will most likely be added to the final design. DISCUSSION.

Purge wells used in the recovery of contaminated groundwater prior to its remediation are at considerable risk from the formation of biofilms. All the conditions to promote in situ growth of microorganisms are present. Biofilms are known to concentrate and accrete material from the water flowing over When this water, as is often the case of in remediation endeavors, contains highly toxic materials, the problems in dealing with the biofilm are magnified. The biofilm and the substrate on which it was found must be considered as new point sources of contamination. The well and its associated plumbing became considerably more dangerous to handle. The products of well cleaning operations must receive special consideration as far as disposal efforts are concerned. Biofilms in nature are known to slough from their substrate. The reasons for this are not well known. If this happens in a purge well, it is possible that the remediation process could be overwhelmed and breakthrough of unremediated material to the effluent could In the B-N location, the benzidine concentration of the biofilm in the well was increased 25 fold over that in the groundwater. This represents a concentration 400,000 times that considered toxic to humans!

Credible chemical analysis of groundwater require that representative samples be taken. In spite of the apparently

facile nature of this task, it is actually very difficult to take a sample of groundwater that accurately reflects its composition. Groundwater samples are usually taken from the effluent of a well. The level of material in this sample represents that in the original sample after it has passed over a long tubular bioreacter, i.e. the well. During the process of moving through the well, its concentration may have been decreased by sorption or, assuming it is biodegradable, metabolism by the biofilm. Microbially-produced products of the original compound may then be found in the well effluent. These compounds may not have been present in the groundwater originally.

CONCLUSIONS AND RECOMMENDATIONS.

- Expect biofouling and plugging problems with purge wells.
- 2. Plan for these problems by considering the design of the well and the construction materials. There are well casings of glass-fiber reinforced plastic that are potentially useful in this regard.
- 3. An effective well maintenance program is essential to keep wells operating.
- 4. Record keeping of well efficiency are important and can predict the need for maintenance of the wells.
- 5. Though further documentation is required, it should be considered that each well involved in the recovery and/or plume control is likely to be a new point source of contamination because of the bioaccumulation around and in the well.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through an Assistance Agreement to the US Army Engineer District, Omaha, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.



ACKNOWLEDGEMENTS

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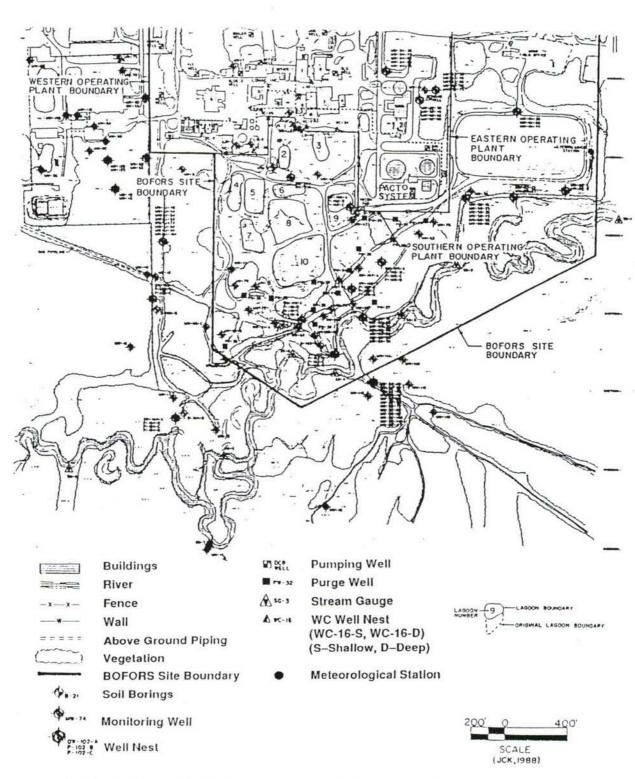
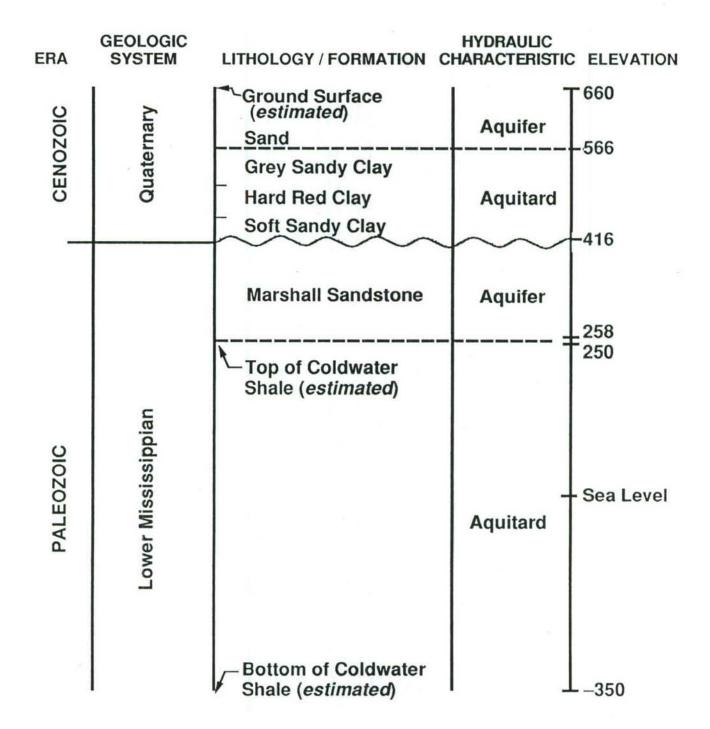


FIGURE 1. SITE LOCATION MAP, MUSKEGON, MICHIGAN





SOURCES:

- WATER WELL RECORD FOR THE ABANDONED DEEP WELL, BOFORS SITE (WELL DEPTH - 245 FT)
- 2. HYDROGEOLOGIC ATLAS OF MICHIGAN



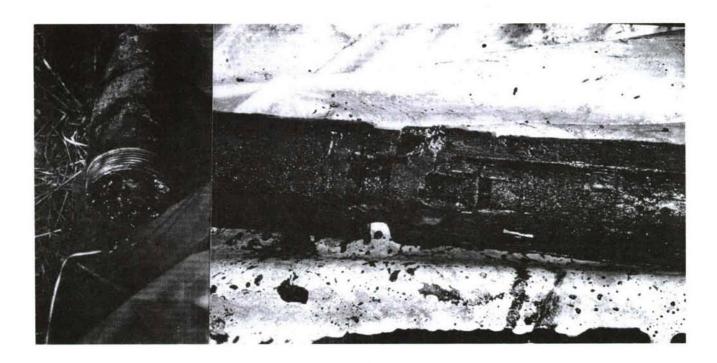


FIGURE 3. CLOGGING OF INTAKE SCREEN AND PIPE



FIGURE 4. CORROSION OF COLLECTOR PIPE

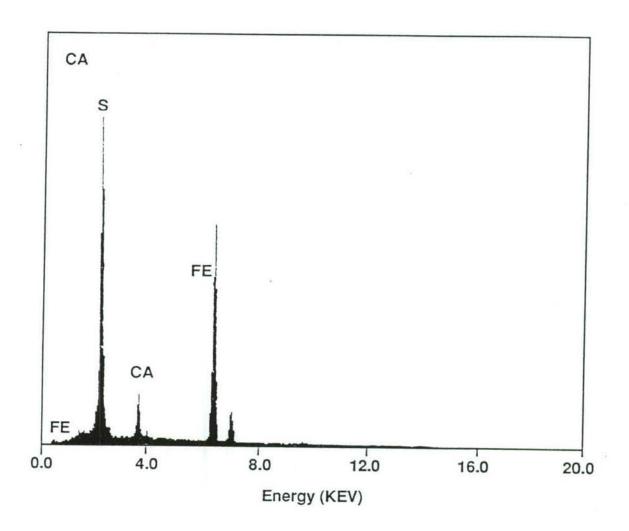


FIGURE 5. X-RAY DIFFRACTION ELEMENTAL ANALYSIS OF WELL SEDIMENT

The Evolution of RAND3D, a Three-Dimensional Solute Transport Ground Water Model, at the U.S. Army Toxic and Hazardous Materials Agency

by Donald Koch, Engineering Technologies Associates, Inc. and Ira May, U.S. Army Toxic and Hazardous Materials Agency

RAND3D is a three-dimensional solute transport ground water model that has evolved under a series of U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) projects. RAND3D is based on the random walk algorithm. The model has been extended to three dimensions and further refined and developed over the last three years by applying it to USATHAMA ground water modeling problems.

The random walk algorithm for solute transport was originally developed at the Illinois Water Survey by Thomas Prickett, Thomas Naymik, and Carl Lonnquist in the 1970's (Prickett, Naymik, and Lonnquist, 1981). Two dimensional solute transport could be simulated including the effects of advection, and dispersion. During the 1980's, Mr. Prickett developed a three dimensional version of the code, as well as enhanced graphics for the two dimensional version.

The random walk algorithm simulates solute transport in an aquifer with a discrete particle analogy. A particle represents a finite mass of solute. This particle is then advected through the aquifer by interpolating between streamlines or pathlines of ground water flow. Dispersion is simulated by random movement of the particles. Figure 1 shows the basic concept of the random walk algorithm. As the number of particles is increased, the particles approximate the continuous distribution of a solute in an aquifer.

The random walk algorithm has several advantages over more direct solutions of the advection-dispersion equation. For a typical ground water contamination problem, it is more efficient. The extent of a contaminant plume is typically rather small in comparison to the area of concern in an aquifer. Traditional Eulerian solutions of the advection-dispersion equation must solve for concentration at all locations in an aquifer. The random walk algorithm only simulates contaminant movement where the contaminant exists in the aquifer. Another advantage is that the random walk algorithm is not subject to numerical dispersion. Numerical dispersion is inherent in finite difference and finite element solutions of the advection-dispersion equation.

The primary disadvantage of the random walk algorithm is the need to use large numbers of particles to get accurate concentrations, especially at the leading edge of the plume. Accuracy (in terms of the exactness of the solution to the advection-dispersion equation) is a function of the number of particles in the simulation. In aquifers with wide ranges of

concentrations, it may be necessary to use large numbers of particles to achieve accuracy.

The current version of RAND3D is based on a three dimensional random walk model and a two dimensional random walk model with a graphical interface both developed by Thomas A. Prickett & Associates. In 1988, USATHAMA tasked Peer Environmental Consultants with Engineering Technologies Associates, Inc. (ETA) and Thomas A. Prickett and Associates as subcontractors to use a three dimensional ground water model to simulate the Building 24 trichloroethylene (TCE) plume at the Picatinny Arsenal, N.J., and to design an efficient pumping plan for controlling the movement of contaminated ground water. A new version of RAND3D was developed for this project.

This new version used the United States Geological Survey Modular Three-Dimensional Finite-Difference Ground-Water Flow Model (MODFLOW) (McDonald and Harbaugh, 1988) for simulating ground water flow. And in addition a new program, PREMOD3D, for calculating ground water velocities from the output of MODFLOW, was developed. MODFLOW was chosen because it may be the most widely used three dimensional ground water flow model in the country. The ability to couple the new solute transport model to a commonly used flow model was considered to be a substantial advantage. When first implemented in 1988, this new version of RAND3D was the only three dimensional solute transport model coupled to MODFLOW in the public domain. Figure 2 shows the data inputs and program sequence for a three dimensional simulation of solute transport.

Another advantage of this system was that flow model calibration and simulation were completely decoupled from the solute transport modeling. MODFLOW could be used without alteration to simulate the head distribution in an aquifer. PREMOD3D was then used to calculate velocities. The resulting velocity file was then used as input to RAND3D.

RAND3D allowed the solute transport simulation to be graphically presented on the computer screen at a user selected scale. The result of this project was both the RAND3D model and an effective extraction well design to control the TCE plume at the Picatinny Arsenal.

Significant features of RAND3D include:

- three dimensional simulation of advection and dispersion of solute in ground water;
- o simulation of linear, reversible adsorption (retardation);
- o simulation of first order decay;
- o unlimited numbers of pollutant sources;



- simulation of solute transport in transient ground 0 water flow (multiple velocity files are created to simulate transient flows);
- mapping of solute concentration in user selected areas of the model, either plan view or cross-section concentration maps may be prepared;
- on-screen display of plume (particle) movement in user selected area, either plan or cross-section views;
- on-screen display of user input geographic features at user selected scale as background for the plume display;
- creation of concentration files for user selected areas of the aquifer for plotting with third party software; and
- the saving and viewing of screens thus creating animation of the plume movement.

This newly developed model was used to design a well layout and pumping plan to prevent the Building 24 TCE plume from reaching a stream which was tributary to a water supply reservoir. The RAND3D model showed that three shallow, water table, pumping wells extracting approximately 100 gallons per minute were adequate to create a hydraulic barrier to the movement of contamination in both the shallow and a deeper The model produced a pumping scheme to accomplish the objective while minimizing the amount of water to be pumped and treated.

The next applications for the RAND3D model were at the Lake City Army Ammunition Plant (LCAAP) in Independence, Missouri and the Louisiana Army Ammunition Plant (LAAP) near Shreveport, Louisiana. Several important modifications were made to RAND3D for these projects. The ability to assign porosity by aquifer and confining layer was added. Simulation of advective movement through nonuniform, sloping aquifers was also added to the algorithm. The aquifers modeled at the Picatinny Arsenal were of glacial-fluvial origin and were relatively flat-lying. LAAP and LCAAP had more complex aquifers with significant slopes. larger areas encompassing significantly different geologic environments were included in these models also. A convergencedivergence algorithm was added to the model to simulate sloping, thinning, and thickening of aquifers. Another modification to the RAND3D and PREMOD3D was adding the ability to simulate water table conditions in lower aquifers. At the Picatinny Arsenal the top aquifer was under water table conditions and the two underlying aquifers were always under confined conditions. both the LAAP and LCAAP, the same aquifers were both water table and confined at different locations. Accurate simulation of this condition required modification of PREMOD3D.

One of the LAAP sites simulated presented a problem for RAND3D. RDX was present in ground water at concentrations ranging from over 20,000 ppb to less than the limit of detection It was not possible to accurately represent this plume with the maximum number of particles currently allowed with RAND3D (10,000). Initial particle weight is calculated as the total mass of contamination divided by the number of particles. Large plumes result in larger particle weights and the resulting limited resolution at the edge of the plume. This problem was solved at the LAAP by using superposition. Solutions to the advection-dispersion equation are linear with respect to concentration. Two solutions to separate problems may be superimposed (added) to yield the solution to another problem. Separate simulations were performed at the LAAP for the one ppb RDX plume and the remainder (one to over 20,000 ppb) of the These results (concentrations) were then added together resulting in the predicted RDX plume extent.

The RAND3D model was chosen for application to the Twin Cities Army Ammunition Plant (TCAAP) in Minnesota. There is significant off-site contamination of aquifers used for municipal water supply and numerous remedial actions have already been implemented. A three dimensional, finite element ground water model (CFEST) had already been chosen for application to this facility. Due to the complexity and size of the CFEST model, the decision was made to use the completed CFEST model to simulate flow and use RAND3D to simulate solute transport.

This decision fully utilized the results of the previous modeling while utilizing the flexibility of RAND3D. Inputs to RAND3D include regularly gridded velocity vectors. These vectors may be obtained from any reasonable source including calculation by PREMOD3D using results from MODFLOW or Darcy's law calculations based on manual mapping of potentiometric surfaces and knowledge of hydraulic conductivity. For the TCAAP ground water modeling, the velocity vectors were calculated from the irregular, three dimensional, quadrilateral finite elements used in the CFEST model.

Another significant modification to RAND3D that was made for the TCAAP project was coupling of models. One of the limitations of RAND3D is the 640K random access memory limit in DOS on an IBM PC computer system. RAND3D is written in Basic. Basic (in all compatible versions) restricts numeric data to 640K of memory. This limitation restricts the grid that may be simulated to 7500 grid cells. Three solutions for this limitation were examined. The first was changing operating systems. OS/2 and Microsoft Professional Basic 7.1 allow Basic programing in protected mode (more than 640K of memory accessible). The second was to rewrite RAND3D to allow variable grid spacing. The third was to allow coupling of models; solute would be transmitted across adjacent model area boundaries. The third solution was chosen for implementation because of its flexibility. Coupling of models allowed models with different grid spacings to be used in

different areas, used the existing well tested algorithm, and avoided performance degradation (good run speed).

The next application of RAND3D for USATHAMA is at the Sharpe Army Depot near Lathrop, California. This facility had numerous small plumes of solvent contamination in ground water. Two ground water extraction systems are currently in operation. The objective of the three dimensional modeling is to design a third ground water extraction and control system that does not interfere with the proper operation of the current two systems. A four aquifer, MODFLOW model has been developed and calibrated. RAND3D is currently being used to design an extraction system at this site.

An ongoing application of RAND3D for USATHAMA is remodeling of the Building 24 TCE plume at the Picatinny Arsenal. The extraction well system designed with the original application of RAND3D has been built. The objective of this project is to verify the model predictions against the actual operating results of the extraction wells. Unfortunately, permitting difficulties have delayed the operation of the system, and no operating results are available to date.

Another objective of the current Picatinny Arsenal project is to update the RAND3D model code. As previously mentioned, RAND3D is written in Basic. This was done to provide the graphical interface in a user friendly computer language. The program was originally compiled with Microsoft Quick Basic Version 3.0. The current version of Quick Basic is 4.5. Unfortunately, the current version (4.5) is not able to compile the RAND3D model. The code will be rewritten using the guidelines of structured programming. Procedures will be coded as subroutines and functions and grouped into functional modules. This approach will allow for compilation with Microsoft Quick Basic Version 4.5. Other modifications planned for the code include:

- o higher resolution screen displays with more colors;
- o faster generation of random numbers;
- o user choice of interpolation algorithm for advective movement;
- o on-screen contouring;
- variable order solute decay; and
- particle splitting to improve computational resolution.

Summary

RAND3D was developed under contract to USATHAMA. It has been and is currently being successfully applied to several Army facilities and accepted by regulatory agencies. It can be made available to all potential Army users. RAND3D is an evolving ground water model which can be used for many ground water problems present at Army facilities. It is a promising tool for the analysis of ground water contamination problems and the cost effective design of ground water remediation systems.

References

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- Prickett, T.A., Naymik, T.G., Lonnquist, C.G., <u>A Random-Walk</u> <u>Solute Transport Model for Selected Groundwater Quality</u> <u>Evaluations</u>, Illinois Water Survey Bulletin 65, 1981.

Figure 1

Basic Concept of Random Walk (from Prickett, Naymik, and Lonnquist, 1981)

Component Random Curves for Dispersion Normal Distribution Component Convective Mean Flow Porous Medium Particle Mean Flow 0000

TRANSVERSE DISPERSION

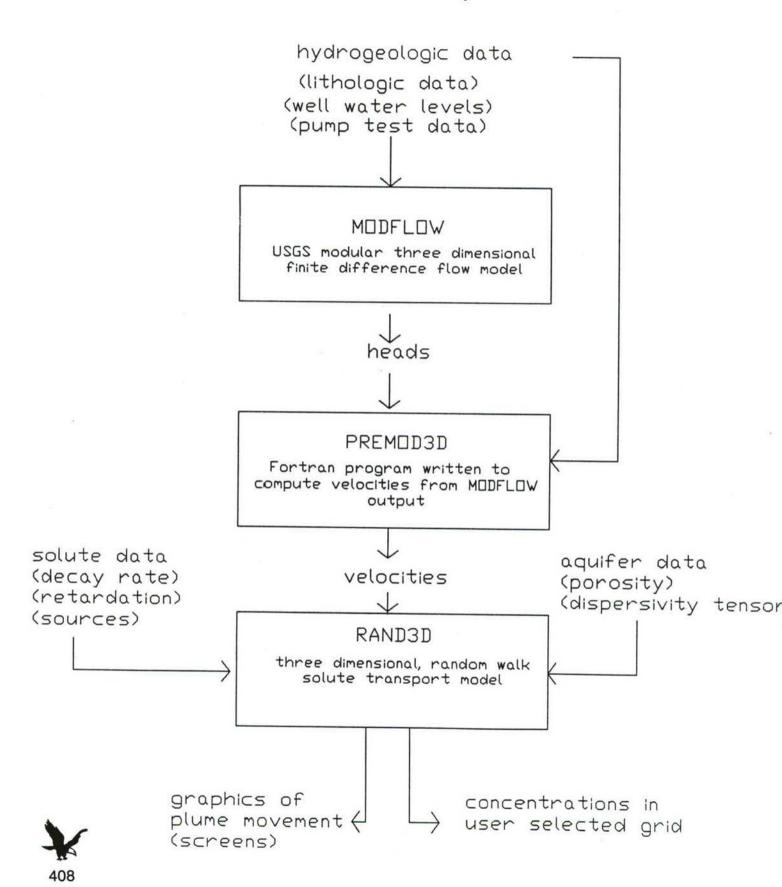
LONGITUDINAL DISPERSION

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Figure 2

Data and Model Sequence



MEETING PART 2 STORM WATER PERMIT APPLICATION REQUIREMENTS FOR THE ARMY'S GROUP APPLICATION

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1. BACKGROUND.

- a. On 16 November 1990, the Environmental Protection Agency (EPA) promulgated final rules (reference 1) for storm water permit applications for "industrial" facilities and established preliminary permitting strategies for industrial activities. Permits are to be submitted to the appropriate State or EPA office by 1 October 1992. The rules will be codified under the National Pollutant Discharge Elimination System (NPDES), reference 4.
- b. Because the definition of an industry in the new rules included sewage treatment plants, recycle sites, scrap yards, and hazardous waste facilities as well as more typical industries such as munitions manufacturing, nearly all Army bases were affected. The applications require one-time runoff characterization at each industrial site.
- c. Realizing the economic stresses the new rules would impose, the USEPA allowed industries to submit group applications if they could show that group members had similar attributes. A key aspect of the group application is that only a representative number of group members need to submit characterization data. The Army submitted a group application (reference 2) consisting of 70 installations (mostly forts under TRADOC and FORSCOM) out of which 10 (Table 1) were selected for storm water runoff characterization.
- d. The United States Army Environmental Hygiene Agency (USAEHA) was asked to complete the characterizations and fill out application forms at each of the 10 installations. The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is handling administrative details (compiling and submitting applications). To date, we have completed the field work at 10 installations and have completed analytical data for six.
- e. The new rules were not always concise or straight forward and left considerable room for professional judgement in decision making. Army-unique facilities did not always fit under the industrial classifications established by the EPA and this caused significant friendly debate among storm water players. That the regulations caused a lot of confusion was illustrated by the number of daily queries we received from the Army community on the subject. In many cases, we sought help from the EPA hotline. Sometimes they helped; often they left us to use our best engineering judgement.
- f. This paper summarizes our efforts to date (analytical data summaries for 7 installations) and we are glad to share our experiences. In the paper, I discuss our methods of selecting sites, monitoring flow, and sampling

runoff. Also, there are some observations on storm water quality findings and some USAEHA literature (reference 3) that may be helpful for anyone filling out application forms.

TABLE 1 PART 2 NPDES PERMIT GROUP APPLICATION REPRESENTATIVE INSTALLATIONS

<u>Installation</u> Fort Belvoir Characterization Period May - June 91

Fort Huachuca

August 91

Fort McCoy

August 91

Fort Wainwright

September 91 and April 92

Fort Drum

October 91

Fort Carson

October - November 91

Fort Polk

December 91

Fort Benning

February 92

Fort Eustis

April 92

Fort Sill

May - June 92

2. SITES DISCUSSION.

- a. <u>Selection</u>. The EPA established 11 categories of industrial sites. Four of the categories were set up according to Standard Industrial Classification (SIC) Codes. The rules listed the industry by Code number only, which led to confusion for installations with no access to the Code identifiers. In particular, the listing of "transportation facilities classified as SIC codes 40, 41, 42, 43, 44, 45 and 5171 which have vehicle maintenance..." was confusing to many army installations because of motor pool inferences. Also, as mentioned before, the Army has a number of activities which do not fit exactly into any of the categories. Each category is discussed below, with a summary of the group application sites.
- (1) Facilities listed in Subpart N of 40 CFR 450-471 (reference 5), subject to new source performance standards (NSPS) or toxic pollutant effluent standards. The key part here is "subject to new source performance standards". Hospitals, for example, are listed under Subpart N, but do not have NSPS or toxic effluent standards and therefore are not subject to storm water regulations. Most of the industries in this category did not apply to forts, except for one metal finishing facility.



NUMBER OF SITES: 1 installation, 1 site

(2) Facilities listed under SIC codes: 24, 26, 28, 29, 311, 32, 33, 3441, and 373. These are large manufacturing industries, none of which apply to forts.

NUMBER OF SITES: 0 installations, 0 sites

(3) Facilities classified under SIC codes: 10, 12, 13, and 14. These are mining categories under which coal mining is listed. We included coal pile storage areas under this category. Two installations already had storm water runoff permits for their coal piles.

NUMBER OF SITES: 2 installations, 2 sites (plus two sites already permitted)

(4) Facilities classified under SIC codes: 20, 21, 22, 23, 2434, 25, 265, 267, 283, 285, 30, 31 (except 311), 323, 34 (except 3441), 35, 36, 37 (except 373), 38, 39, and 4221-4225. These are all manufacturing industries, but include a "warehousing and storage" category, which might apply to many forts. However, a facility under these codes is subject to the storm water rules only if stored materials are exposed to precipitation. This differs from the first three categories in that the first three are subject to the rules regardless of where materials are stored. No installation we visited had outside warehousing of materials.

NUMBER OF SITES: 0 installations, 0 sites

(5) Transportation facilities classified under SIC codes: 40, 41, 42 (except 4221-4225), 43, 44, 45 and 5171 which have vehicle maintenance shops, equipment cleaning operations, or airport deicing operations. This category was the most confusing and led to disagreements in site selection. These codes specifically include airfields (45), marinas (44), railroads (40), and bulk petroleum facilities (51). The codes do not specifically include automobile repair facilities. Code 41 is "local and suburban transit and interurban highway passenger transportation", which comes the closest. The preamble to the rules discusses SIC Code 75: "Automotive Repair, Services, and Parking" and specifically excludes the group because the Clean Water Act (CWA) requires the EPA to address this category under studies mandated by the Act. Every fort has dozens of motor pools where fleets of all types of vehicles are maintained. We included only motor pools where bus and taxis are maintained because these loosely fit into the SIC Code 41. We also sampled at very large tactical vehicle sites (tanks) and a few sites specifically requested by the installation to be included. It should be noted that the EPA may only be postponing its decision to incorporate automotive repair shops until the required studies are performed. So, the motor pools may eventually be subject to the regulations.

NUMBER OF SITES: 7 installations, 19 sites

(6) Hazardous waste (HW) treatment, storage, or disposal (TSD) facilities. This category led to further debate, since the rules' preamble

this site, and the runoff was uncollectible.

- (c) Permeable and Vegetated Sites. A great number of sites generated no runoff because the conditions on the site (such as plant growth) precluded runoff formation. Many old, closed (but not to RCRA standards) landfills were completely overgrown with grasses, trees and weeds. Rainfall soaked into the ground and was taken up by the vegetation; no runoff occurred ran off. In some cases we collected grab samples where water ponded or seeped out of hill sides after a heavy rain. At other sites vegetation reduced runoff to small amounts or eliminated it altogether. Sewage treatment plants often fell into this category. Thirteen sites (not including the small sites discussed above) generated insufficient runoff to measure. In some cases, we collected grab samples at low spots because there was no runoff.
- (d) Flat Sites. Another type of site was one often in a flat main cantonment area. Some of these sites had underground collection systems, but most did not. Most of these types had no recognizable flow runoff pattern. Generally, at these sites rainwater either: (1) ran off the site in shallow sheets to adjacent grassy areas where percolation occurred, or (2) ponded on the site at low spots. Several smaller motor pools and HW storage buildings often had sites with these runoff characteristics. At one airfield, runoff crossed a large grassy area in sheets and percolated into the grassy zone. Again, in some instances we were able to collect grab samples in ponded areas.
- 3. FLOW MONITORING. The permit application requires that flow be measured or estimated at each site. Measuring flow presented many unique challenges, both prior to and during the rain events. Fortunately, we boast a full complement of monitoring equipment and maintain experience in their use. Where runoff did occur, we measured the flow at 39 sites (7 installations) and used textbook runoff coefficients to estimate flow at 15 other sites. Additionally, we are estimated season-long snow melt runoff at the Alaska site, Fort Wainwright.
- a. At fifteen sites, we installed a V-notch weir across a runoff channel just outside the site in question. We attached a pre-cut metal "V" (30, 45, 60 degree) to a piece of plywood cut to fit the width of the channel. Plywood cuts were made onsite with electric saws powered by a portable generator. The weir was attached using self tapping screws. Flow over the weir was then measured using either a bubbler-type or ultrasonic-type flow recorder. The recorders were powered by 12-volt automobile (DC) batteries.
- b. At eight sites, we placed a V-notch weir across a culvert inlet or outlet similar to the set-up above. In these cases, we normally sealed the weir against the culvert with clay. Because some secure sites prevented 24hour access, we had to place several of the weirs at culvert outlets. To prevent water pressure from blowing out the weir during the runoff event, we braced the weirs with 2 by 4's.
 - c. At seven sites, storm water flowed into underground drains and out to



receiving waters via free falling pipe outfalls. Here, we used V-notched inserts. The inserts were either metal band (expandable to fit snugly) or precut metal "V"s attached to round cut plywood (cut onsite) and inserted into the pipe. We sealed both types with silicon or clay.

- d. At five sites, a V-notch weir (as in paragraph 3.a. above) was placed across a manhole channel and sealed with clay.
- e. Other types of flow monitoring included a rectangular plywood weir set-up across a wide stream and a Palmer-Bowlus flume inserted into a manhole channel.
- f. At fifteen sites we used either a hydraulics textbook runoff coefficient or a runoff coefficient derived from similar sites we measured flow at, to estimate runoff quantities. The coefficient was multiplied by the area of the site and the amount of precipitation falling on the site. This product was converted to gallons. Flow had to be estimated at these sites for a number of reasons: flow monitoring equipment failed during the rain event, sites were too large or too inaccessible (many landfills) to adequately measure flow, or runoff from the site occurred in sheet flow and there was no discernable runoff channel to measure flow in.
- g. As mentioned before, most sites had more that one runoff location. We measured flow at as many of the locations as possible and where impractical we used the available flow data and interpolated to cover the entire site. Also, the maximum-rate to average-rate ratio at a monitored site was used to estimate maximum flow rates (needed on the application) at similar unmonitored sites.
- h. We found that where we measured flow, the anticipated runoff coefficient was higher than the measured one. Runoff coefficients for sites which were substantially (>75%) paved typically averaged 0.2 0.3. We believe that the interception portion of runoff at these sites was significant, particularly at low rainfall amounts. Puddling was very noticeable on most paved areas. Also, asphalted areas allow water to percolate. At higher rainfall levels, percolation rates were lower and the interception portion was less significant. Generally, the more rain falling on a site, the higher the runoff coefficient. We do not have enough data for a good analysis, but the point to be made here is that standard runoff coefficient tables are to be used carefully. Factors to consider include amount of vegetation on the site, relative wetness of the ground, season (winter soil might be frozen and rain will run off more than summer soil), amount of rainfall, relative slope of the site, and type of pavement (asphalt versus concrete).

4. SAMPLING.

a. The rules require that a grab sample be collected for all parameters during the first 30 minutes of the runoff period (or as soon as possible after the beginning of the period) and that a flow weighted composite also be collected for all parameters (except oil and grease, pH, chlorine residual and fecal coliform) over the entire runoff period or for the first 3 hours of the

event.

- b. Automated sampling equipment simplified meeting storm water composite sampling requirements. We set up samplers at each site and powered them using 12 volt, DC, automotive batteries. The samplers came on when water touches a conductivity probe (called an actuator). A typical, simplified, step by step set-up follows:
- (1) The sampler is programmed to collect two, 1000 mL samples every 15 minutes. There are 24 bottles in the sampler base. All bottles would be filled during a 3 hour runoff event.
- (2) An actuator is connected to the sampler and placed in the runoff channel. The actuator is usually attached to a stake and positioned in the channel an inch or so above the channel floor, but slightly above the sampler tubing to ensure that the sampler collects a sample. The sampler is then programmed to recognize the actuator and goes into a stand-by mode.
- (3) When runoff touches the probe, the sampler begins sampling. If the runoff event is short-lived and the water level drops below the probe, the sampler will shut off.
- c. Since the sampler collected time sequential samples, a flow composite is manually formed using the sequential samples and the flow record from the site. Proportions of the samples are poured into the compositing container according to the flow rate at the time of collection.
 - d. We collected grabs onsite during the rain event.
- e. Grabs and composites were placed into individual containers, preserved as specified in 40 CFR 136 (reference 6) and shipped to USAEHA labs for analysis.
- 5. EVOLVING SAMPLING PROCEDURES. During the course of the storm water studies we faced all types of problems. No study went off without a hitch. Each successive study had fewer problems as we refined techniques and learned from the previous study. Despite problems as ranging from watching flawed weather forecasts to soaking paper notebooks (we now have waterproof notebooks) during heavy downpours, we were able to complete the studies. Some of the problems we encountered are discussed below.
- a. Actuator Does Not Actuate. Occasionally, the actuator did not turn on the sampler, even if its operation was checked using clean water during setup. We believe that the conductivity of runoff is sometimes to low to initiate the actuator. Deionized water will not trigger the actuator. Also, we think that an air bubble can form under the rain shield and prevent the actuator from working. To prevent this, we mounted the actuator at a 45 degree angle from the ground. Finally, we always visited sites during the rain event to check on equipment.
- b. <u>Sediment Buries Actuator and Collection Tubing</u>. In some earthen ditches, dirt erodes off and settles out around the actuator and tubing,



rendering both inoperable. Sometimes the sampler will draw dirt into its tubing, partially clogging it and causing a vacuum in the tubing. The tubing invariably pops out of its connection with the sampler. If sedimentation appeared to be a possibility, we placed a rock or screen barricade around the tubing and actuator and checked the site often.

- c. Weir Washout. This phenomenon was common in earthen ditches during heavy rains. Carry a shovel with you during your site checks to plug leaks in leaking weirs. Note approximate percent of flow lost in washout areas.
- d. Weir Leak. Again, weir leaks were common in earthen ditches and are also likely anywhere you have sealed weirs in place. Plug the weirs as well as you can during the rain event and note the approximate amount of leakage. Check cemented connections regularly during dry periods. As clay dries it has a tendency to contract and pull away from the contacting surface.
- e. Weir Overflow. Heavy rainfall may cause runoff to overtop the weir. The recorder will continue to track the level in most cases, but the flow equation that the meter is using will not be correct. Note approximately when the overtopping began and the approximate level above the weir. You will have to estimate the additional flow using a rectangular weir approximation. Make your weir as large as possible in your initial set-up.
- f. Stolen Equipment. This has not been a problem. In high traffic areas, we placed orange traffic cones around the equipment with warning tape and a phone number to call for information. Put your batteries inside a plastic bag. Also, notify the Military Police about your sites. They will normally provide regular surveillance.
- g. Stuck Distributor Arm. If you inadvertently program more than 1000 mL into individual bottles, the overflow will pool in the base of the sampler. This may cause the empty containers to float slightly and subsequently causes the distributor arm to get hung up on a bottle. Make sure that the inside tie-downs are secure and double check your programmed pull.
- h. Other tips. Use a waterproof notebook to keep your records in. Write down all programmed values in case the settings are inadvertently changed or vandalized. Check the voltage of your batteries daily. The samplers will not draw much current as they are in a stand-by mode. The flow meters run continuously and draw more current. You can extend battery life by turning off the flow meters until a rain event is imminent. Make sure you pack plenty of flashlights for night rains.
- 6. STORM WATER QUALITY SUMMARY. Appendix B contains ambient water quality criteria which was use for storm water comparisons. In most cases, these criteria are the most stringent. It should be stressed, however, that these criteria were generally developed using under worst case stream flow (such as 10 year, 7 day average low flow) conditions. The EPA has not decided how it will approach water quality criteria for storm water conditions when the receiving water is not at low flow conditions.
 - a. Oil and Grease. Oil and grease concentrations were not high overall.

Only 5 samples had levels exceeding 10 mg/L. The median concentration was about 1.5 mg/L. High levels at the 5 sites can be attributed to poor site maintenance. Unmitigated petroleum product spills were noted at each site with high levels.

- b. Total Suspended Solids (TSS). As expected, suspended solids loads in storm water runoff were high. The median grab TSS concentration was 100 mg/L and reached 3800 mg/L in one sample. Composites had better quality, with a median concentration of 53 mg/L. Using 30 mg/L (secondary treatment definition) as a criteria, 70-75% of the sites would not comply. An average installation would contribute tons of sediment annually from its industrial sites alone. Some site housekeeping measures (such as sweeping grounds regularly) may improve TSS levels in runoffs. However, many of the sites are inherently dirty (motor pools, DRMO yards) or are dirt (OD grounds) and ground cleaning would be ineffective. Construction of detention ponds or use of other solids management techniques may offer the best reduction method for many sites.
- c. BOD₅ and COD. BOD₅ levels were high in only a few instances and the median level was only 5 mg/L. Only 7 sites would not comply with a 30 mg/L criteria (secondary treatment) for grabs and only 3 composite samples exceeded 30 mg/L. Extremely high levels of BOD₅ were associated with significant quantities of oil and grease at two motor pools. COD concentrations were low in general also, though an average BOD₅/COD ratio of about 0.1 suggests an elevated presence of biologically resistant organic material (such as oily matter). The highest levels of COD were found at sites with high levels of oil and grease. This suggests that COD levels are related to petroleum materials on site. Grabs (61 mg/L median) were typically worse than composites (42 mg/L median). If COD levels are related to oily material, then improved spill cleanup is warranted. We noted that many parked vehicles at motor pools had small leaks of lubrication fluids.
- d. <u>Nutrients</u>. Ammonia-nitrogen and nitrate-nitrogen levels were not significant overall. Median levels of ammonia (as total Kjeldahl nitrogen) and nitrate were 1.1 mg/L and 0.5 mg/L, respectively in grabs and 0.9 mg/L and 0.5 mg/L, respectively, in composites. Higher levels were associated with STP's and old landfills. Nitrogen levels in STP runoff appear to be related to sludge handling operations and conditions such as over-spray from trickling filter arms. Both conditions are correctable through improved onsite maintenance. Elevated phosphorous levels were low on average, but many sites had levels in excess of 1.0 mg/L. Twenty-five percent of the grabs and 12% of composites exceeded 1.0 mg/L, a typical limit for discharges into high quality waters. Higher P levels were associated with STP's and DRMO's. STP sources are readily apparent (over-spray, sludge handling); DRMO sources are not. However, at both types of sites improved material management may yield lower P levels in runoffs.

e. Metals.

(1) Iron and Aluminum. These two metals were consistently high in both grab and composite runoff samples. The median iron concentration in grab



and composite samples was 3.7 mg/L. The median aluminum level was 5.5 mg/L in grabs and 5.8 mg/L in composites. EPA water quality criteria (fresh water chronic) for iron is 1.0 mg/L. Approximately 70% of the grabs and 80% of the composites exceeded 1.0 mg/L of iron. The EPA fresh water criteria for aluminum is 0.75 mg/L (one-hour average). However, the toxicity of aluminum is very pH dependent; the substance is more toxic at lower pH levels. Nearly all of the sites with high aluminum and iron levels in runoff had metal products on site exposed to rain: shattered munition casings on OD grounds, scrap metal and a wide assortment of metal products at DRMO yards, aluminum cans at recycle centers, and parked vehicles at motor pools. However, iron and aluminum compounds are often prevalent in soils. Sites with high suspended solids levels in runoff also had correspondingly high iron and aluminum levels. This suggests that controlling suspended solids through devices such as detention ponds or other erosion control methods will also lead to improved iron and aluminum residuals.

- (2) Zinc, Lead, Copper. The EPA fresh water organism chronic water quality criteria are for these metals are 0.12 mg/L, 0.083 mg/L, and 0.018 mg.L, respectively. Sixty percent of all samples exceeded the copper criteria, 55% exceeded the zinc criteria, and 30% exceeded the lead criteria. Nearly all of the sites were either DRMO yards, HW TSD sites, OD grounds, or airfields so there is some correlation between what is on the site and what appeared in runoffs. For example, the DRMO yards and HW TSD sites had unserviceable battery storage areas which may have led to increased lead levels in the runoffs. OD grounds may have higher metal compounds because of metal casing debris and also potentially because some munitions have lead as a component.
- (3) Other Metals. Antimony, arsenic, beryllium, cadmium, chromium, mercury, nickel, selenium, silver, thallium, and zinc were analyzed in 90 samples. Of 990 analyses, only about 2% exceeded water quality criteria and all of these were silver, cadmium, or chromium. Only one cadmium at 0.092 mg/L from an airfield runoff sample exceeded criteria by more than a factor of 10.
- f. <u>Volatiles</u>, <u>Semi-Volatiles</u>, <u>and Pesticides</u>. We sampled 60 sites for volatiles and semi-volatiles and 44 sites for pesticides/herbicides (see list in Appendix C). Samples from 7 sites had levels of volatiles/semi-volatiles above their detection limits. These are summarized in Appendix D. Most of the detected compounds are associated with petroleum products and, except for one site, all compounds were below water quality criteria. However, their

²It should be stressed again that the water quality criteria are for ambient conditions. Runoff from any of the discussed sites would be diluted upon entering receiving streams. This dilution factor would have to be considered by regulating bodies if numerical runoff limits are imposed. For example, a 10:1 dilution factor at any of the sites would reduce the number of exceedances for copper to 11%, for lead to 0%, and for zinc to 4%.

presence in any sample should be investigated and their source eliminated. At the worst site (an engine test facility) 10 compounds were detected. A berm directing runoff to an oil water separator was broken. Runoff was partially by-passing the separator to a surface ditch. Had the berm been intact, all contaminated runoff at this site would have been directed through the separator and into the sanitary sewer system. The separator was a good idea, but site maintenance was poor.

- g. <u>Composite versus Grabs</u>. The rules require composite and grab sampling because of the "first flush" theory that initial runoff should carry the highest pollutant load and later runoff would be less contaminated as materials are washed from the site. Our sampling supports this finding, except for metals. Most composite samples were of better quality than grabs. For example, the median levels of total suspend solids in grabs was 100 mg/L while the median level of TSS in composite samples was 53 mg/L. However, median zinc, copper, lead, iron, and aluminum concentrations in composite samples were equal to or higher than median concentrations in grab samples. This might suggest that metal materials at each site are contributing pollutants throughout runoff periods.
- 7. SUMMARY. USAEHA provided the field sampling expertise for one of the Army's Part 2 NPDES permit group applications for storm water runoff at industrial sites. No part of the process was straight forward from selecting sites, to collecting samples, measuring flow, or filling out EPA applications. We used significant amounts of professional judgement in interpreting the rules. The result has been an advancing of the art of storm water runoff characterization. Water quality data indicates that most sites will have to deal with managing solids in the runoff and some sites will have to manage some elevated metals. Improvements can also be made in site cleanliness. For further sampling and monitoring help, we have put together Water Quality Information Paper #37, Sampling Protocol for Storm Water Permit Application. Call Michael Robison or William Fifty at DSN 584-3289 or commercial 410-671-3289 for a copy or for assistance.

APPENDIX A REFERENCES

- 1. Final Rule, National Pollutant Discharge Elimination System Permit Application Regulations for Storm Water Discharges, 55 Federal Register (FR) 47990, 16 November 1990, with revisions.
- 2. Memorandum, DS OCE, ENVR-EP, 31 May 1991, subject: National Pollutant Discharge Elimination System Permit for Storm Water Discharges Group Application Part 2.
- 3. Water Quality Information Paper # 37, USAEHA, National Pollutant Discharge Elimination System, Sampling Protocol for Storm Water Permit Applications, 21 April 1992.
- 4. Title 40, CFR, Part 122, EPA Administered Programs, The National Pollutant Discharge Elimination System.
- 5. Title 40, CFR, Subpart N, Effluent Guidelines and Standards.
- 6. Title 40, Code of Federal Regulations (CFR), Part 136, latest revision, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
- 7. Integrated Risk Information System (IRIS), USEPA, September 1990.
- 8. Quality Criteria for Water, United States Environmental Protection Agency (USEPA), 1992
- 9. 40 CFR Parts 141 and 143, National Primary and Secondary Drinking Water Regulations.

APPENDIX B CRITERIA USED TO EVALUATE RUNOFF QUALITY

D	C1#1-	C
Parameter	Criteria	Source
Ammonia	1.0 mg/L	Typical Permit Limit
Phosphorous	1.0 mg/L	Typical Permit Limit
Aluminum	0.75 mg/L	EPA Chronic Water Quality
		Criteria (WQC)
Iron	1.0 mg/L	EPA Chronic WQC
Lead	0.0032 mg/L	EPA Chronic WQC
	0.083 mg/L	EPA Acute WQC
	0.05 mg/L	Drinking Water Maximum Contaminant
÷		Level (MCL)
Antimony	0.03 mg/L	EPA Chronic WQC
Beryllium	0.0053 mg/L	EPA Chronic WQC
Cadmium	0.0011 mg/L	EPA Chronic WQC
	0.005 mg/L	Drinking Water MCL
Chromium (total)	0.210 mg/L	EPA Chronic WQC
	0.10 mg/L	Drinking Water MCL
Copper	0.012 mg/L	EPA Chronic WQC
	1.3 mg/L	Drinking Water MCL (proposed)
Mercury	0.000012 mg/L	EPA Chronic WQC
	0.0024 mg/L	EPA Acute WQC
	0.002 mg/L	Drinking Water MCL
Nickel	0.160 mg/L	EPA Chronic WQC
Nitrate	10.0 mg/L	Drinking Water MCL
Silver	0.00012 mg/L	EPA Chronic WQC
	0.004 mg/L	EPA Acute WQC
Thallium	0.04 mg/L	EPA Chronic WQC
	1.4 mg/L	EPA Acute WQC
Zinc	0.110 mg/L	EPA Chronic WQC
		Section and the section of the secti
Trichlorofluoromethane	None	
Toluene	17.5 mg/L	EPA Acute WQC
	1.0 mg/L	Drinking Water MCL
Chloroform	1.2 mg/L	EPA Chronic WQC
Anthracene	0.00003 mg/L	IRIS (Health Risk)
Naphthalene	0.620 mg/L	EPA Chronic WQC
1,2,4 trimethylbenzene	0.050 mg/L (benze	ne) EPA Chronic WQC
1,2 dichloroethane	20.0 mg/L	EPA Chronic WQC
	0.005 mg/L	Drinking Water MCL
Acenapthene	0.52 mg/L	EPA Chronic WQC
Phenanthrene	0.0063 mg/L	EPA Chronic WQC
1,2,3 trichlorophenol	0.244 mg/L (di)	EPA Chronic WQC
Xylene	10.0 mg/L	Drinking Water MCL
A CONTRACTOR OF THE PROPERTY O	Control of the Contro	CONTRACTOR OF THE PROPERTY OF

APPENDIX C VOLATILE AND SEMI-VOLATILE COMPOUNDS PESTICIDES/HERBICIDES

GC/MS	Fraction	Volatiles	Compounds
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	GC/MS Fraction Volatiles Compound	s
Acrolein	Dichlorobromomethane	1,1,2,2,-Tetrachloroethane
Acrylonitrile	1.1-Dichloroethane	Tetrachloroethylene Toluene 1,2-Trans-Dichloroethylene
Benzene	1,2-Dichloroethane	
Bromoform	1,1-Dichloroethylene	
Carbon Tetrachloride	1.2-Dichloropropane	1,1,1-Trichloroethane
Chlorobenzene	1.3-Dichloropropylene	1,1,2-Trichloroethane
Chlorodibromomethane	Ethylbenzene	Trichloroethylene
Chloroethane	Methyl Bromide	Vinyl Chloride
	Methyl Chloride	
2-Chloroethylvinyl Ether	Methylene Chloride	
Chloroform	Acid Compounds	
	PROPERTY OF TAXABLE PROPERTY.	Pentachlorophenol
2-Chlorophenol	2,4-Dinitrophenol	Phenol
2,4-Dichlorophenol	2-Nitrophenol	2.4.6-Trichlorophenol
2,4-Dimethylphenol	4-Nitrophenol	2,4,0-111011010
4,6-Dinitro-O-Cresol	p-Chloro-M-Cresol	
	Base/Neutral	
Acenaphthene	2-Chloronaphthalene	Fluroranthene
Acenaphthylene	4-Chlorophenyl Phenyl Ether	Fluorene
Anthracene	Chrysene	Hexachlorobenzene
Benzidine	Dibenzo(a,h)anthracene	Hexachlorobutadiene
Benzo(a)anthracene	1,2-Dichlorobenzene	Hexachloroethane
Benzo(a)pyrene	1,3-Dichlorobenzene	Indeno(1,2,3-cd)pyrene
3,4-Benzofluoranthene	1,4-Dichlorobenzene	Isophorone
Benzo(ghi)perylene	3,3'-Dichlorobenzidine	Napthalene
Benzo(k)fluoranthene	Diethyl Phthalate	Nitrobenzene
Bis(2-chloroethoxy)methane	Dimethyl Phthalate	N-Nitrosodimethylamine
Bis(2-chloroethyl)ether	Di-N-Butyl Phthalate	N-Nitrosodi-N-Propylamine
Bis(2-chloroisopropyl)ether	2,4-Dinitrotoluene	N-Nitrosodiphenylamine
Bis(2-ethylyhexyl)phthalate	2.6-Dinitrotoluene	Phenanthrene
4-Bromophenyl Phenyl Ether	Di-N-Octylphthalate	Pyrene
Butylbenzyl Phthalate	1,2-Diphenylhydrazine (as Azoben- zene)	1,2,4-Trichlorobenzene
	Pesticides	
Aldrin	Dieldrin	PCB-1254
Alpha-BHC	Alpha-Endosulfan	PCB-1221
Beta-BHC	Beta-Endosulfan	PCB-1232
Gamma-BHC	Endosulfan Sulfate	PCB-1248
Delta-BHC	Endrin	PCB-1260
Chlordane	Endrin Aldehyde	PCB-1016
4.4'-DDT	Heptachlor	Toxaphene
4,4 501	Heotachlor Enoxide	

Heptachlor Epoxide

PCB-1242

4,4'-DDE

4,4'-DDD

APPENDIX D Volatiles and Semi-volatiles Detected During Storm Water Sampling

Installation/Site	Compound	Concentration
		(micrograms per liter)
Fort Drum		
Airfield (grab)	Trichlorofluoromethane	7
(composite)	Trichlorofluoromethane	6
Fort Polk	Te.	
South STP (grab)	Toluene	6
	Chloroform	1
North STP (grab)	Toluene	9
Motor Pool (grab)	Anthracene	21
Motor Pool (grab)	Naphthalene	8
	1,2,4 trimethylbenzene 1	
(composite)	Naphthalene	7
Fort McCoy		
	ab) 1,2 dichloroethane	8
Fort Benning		ě.
Engine Test Area	Naphthalene (composite)	16
	(grab)	46
(grab)		200
	phenanthrene	60
	p-isopropyltoluene	3
	m & p xylene	5
	o-xylene	4
	fluorene	25
	acenapthene	22
	1,2,4-trimethylbenzene	7
	1,2,3-trichloropropane	27

PHOTOCATALYTIC DECOMPOSITION OF NITROGLYCERINE-CONTAMINATED AIRBORNE VOCs¹

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ABSTRACT

Advanced oxidation methods involving photocatalytic decomposition of hazardous organic wastes by the use of semiconductors, in general, and TiO2, in particular, has received much attention recently. At Florida Solar Energy Center, we have developed many photocatalytic systems using both natural sun light and artificial radiation for detoxification of aqueous as well as airborne hazardous organic contaminants. This paper describes a new process for photocatalytic purification of volatile organic compounds (VOCs) containing hazardous levels of airborne nitroglycerine (NG). The design and fabrication of several bench-scale, continuous flow reactors that employ commercially available low-cost, low-pressure, mercury ultraviolet lamps are given. Special techniques developed for the safe handling and simulation of waste streams containing energetic compounds are also discussed. In general, we observed very high destruction and removal efficiencies for the titaniabased photocatalytic processes compared to those obtained from the photolytic (no catalyst present) systems. Our findings indicate that a properly designed photocatalytic system can effectively and efficiently mineralize airborne organics containing energetic compounds without a need for expensive and sophisticated UV light sources (e.g. pulse xenon arc lamp) and/or added active oxidants (e.g. H₂O₂, O₃, etc.). Process energy requirement of 163 W/SCFM of air input was determined for detoxification of airborne nitroglycerine under realistic process conditions. Results from the artificial light experiments are being used to develop a solar-driven photocatalytic system for the treatment of munitions-type waste streams.

Introduction

The explosive/propellant manufacturing processes involve the use of solvents such as acetone and ethanol for their formulation. When solvents are sparged at various process

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stages, using hot air, significant levels of airborne volatile organic compounds (VOCs) containing energetic chemicals are emitted. For example, the multibase propellant production processes employ mixer and forced air dry (FAD) unit operations. The effluent streams from these operations contain in excess of 1200 ppmv of acetone, 1800 ppmv of ethanol and 10 ppmv of nitroglycerine (NG) in air.

Photochemical processes offer a viable alternative to the use of high temperature incineration or physical separation techniques for the treatment of hazardous organic compounds HOCs in both aqueous and gaseous media. Many photochemical processes have been developed and successfully applied to the destruction of hazardous organic compounds. These processes utilize both natural (sunlight) and artificial (mercury and xenon lamps) light sources to promote various free-radical oxidation reactions. Generally, a source of ultraviolet (UV) radiation is used either directly or in the presence of an active photocatalyst to drive chemical reactions. The commonly used low-pressure mercury lamps are simple, inexpensive and highly efficient source of UV radiation. Unfortunately, almost all the radiation emitted by these lamps is resonance radiation of mercury vapor at wavelengths of $\lambda 254$ nm and, to much lesser extent, $\lambda 185$ nm. On the other hand, a vast majority of HOCs of interest absorb light at wavelengths below 300 nm. In order to achieve practical destruction and removal efficiencies (DRE) for HOC detoxification by noncatalytic photolysis using low-pressure mercury lamps, it is often necessary to use added active oxidants such as ozone or hydrogen peroxide. In the presence of $\lambda 254$ nm radiation and either ozone or hydrogen peroxide, heterolytic cleavage of O-O bonds readily takes place producing active hydroxyl (OH), HO₂-superoxide, and others free radicals. The OH radical is especially reactive and attacks most HOCs. After primary reaction with OH radicals, HOCs, more easily, undergo oxidative degradation in the presence of oxidants and even molecular oxygen, i.e.

$$H_2O_2 + hv \rightarrow 2OH$$

 $O_3 + H_2O + hv \rightarrow 2OH + O_2$
 $RH + OH \rightarrow R + H_2O$
 $R + O_2 \rightarrow RO_2 \rightarrow \rightarrow CO_2$

In an effort to do away with the requirement for added oxidants, more recent applications have used sophisticated xenon plasma flashlamps to generate light in the deep UV region ($<\lambda250$ nm) (1). Unfortunately, this type of light source is intrinsically more complicated and costly and has lower efficiency (electrical to UV energy conversion) and shorter lamp life span than the conventional mercury-based UV lamps. Main advantage of the pulsed xenon arc lamps is their ability to produce high intensity, continuous spectrum, radiation which extends to deep UV region.

To avoid the difficulties encountered with UV photolysis techniques and eliminate the need for added oxidants or the use of highly sophisticated deep UV light sources, photocatalytic oxidation methods are increasingly used for the treatment of both aqueous and gas-phase HOCs. Photoelectrochemical methods rely on the use of special semiconductor

photocatalysts to promote chemical reactions. Upon irradiation of the catalyst, electron/hole pairs are generated on the semiconductor surface with free electrons (e⁻) produced in the conduction band and positive holes (h⁺) occupying the valence band. For an n-type semiconductor, the holes migrate to the catalyst surface and act as strong oxidizing agents that can react with species present in various ways. Both the electrons and holes are capable of promoting HOCs degradation reactions. For example, conduction band electrons (e⁻_{CB}) can reduce molecular oxygen to reactive radicals,

$$e_{CB}^{-} + O_2 \rightarrow O_2^{-} \rightarrow H^{+} \rightarrow HO_2^{-} \rightarrow (-\frac{1}{2}O_2) \rightarrow \frac{1}{2}H_2O_2 \rightarrow OH^{-}$$

The valence band holes (h+vB) can oxidize water to produce hydroxyl radicals.

$$h^{+}_{VB} + H_2O \rightarrow H^{+} + OH^{-}$$

The net effect is generally complete oxidation and full mineralization of HOCs.

In this paper, we describe a photoelectrochemical method involving the use of ultraviolet radiation from low-pressure mercury lamp and TiO_2 (anatase) photocatalyst for the treatment of airborne VOCs. We employed simulated waste streams that contained acetone, ethanol and nitroglycerine at levels normally encountered in emissions from the munitions production facilities. The ultimate objective of this work is to design and build a cost effective detoxification system for abating airborne VOC emissions from the explosive/propellant manufacturing processes.

Background

Much work has been carried out on the photocatalytic decomposition of organic pollutants (e.g., pesticides, halogenated aliphatics, phenols and surfactants) in water (2-4). However, very few studies are available which address photochemical detoxification of HOCs in the vapor-phase (1,5,6). As far as the NG-contaminated, airborne VOCs are concerned, no photoassisted process has been reported in the literature.

In principle, the gas-phase photodestruction processes do not differ from those occurring in aqueous media. Although, the photochemical and mechanistic aspects of both systems are very similar, there can be substantial differences in the nature of the reaction products. Gas-phase photo-reactions involving HOCs can be one of three classes, namely, homogeneous photolysis in the presence and/or absence of added oxidants, and photocatalytic oxidation.

There are certain differences between homogeneous photolysis of VOCs in the gaseous and aqueous media. The photo-splitting reactions occur more readily in the gaseous phase since there are no "cage" like effects that occur in the presence of solvents and affect the efficiency of the photoprocess and product distribution.

The photophysics and photochemistry of semiconductors used in the photoelectrochemical (PEC) systems are complicated and discussed elsewhere (7). Very briefly, the extent of PEC reactions is determined primarily by the electronic (band-gap) characteristics of the semiconductor and the standard potentials of the redox couple in the solution. Depending upon the prevailing conditions, a given electron/hole (e⁻/h⁺) separation process can last from only few nano-seconds to several hours (8). The recombination of e⁻/h⁺ pairs can also take place, resulting in reduced quantum efficiency of the process. The recombination can occur either between the energy bands or on the semiconductor surface. To mitigate this problem, conducting materials such as noble metals (i.e. Pt) and certain metal oxides (i.e. RuO₂) have been used to facilitate electron transfer and prolong the lifetime of the e⁻/h⁺ separation process.

Photoelectrochemical systems have the advantage of flexibility and comparatively higher process efficiencies over homogeneous photolysis methods. This factor becomes even more important when a mixture of different types of VOCs are present. In that case, the combination of ultraviolet (UV) light and the photocatalyst form new routes for the simultaneous degradation of these compounds (e.g. photoreduction by conduction band electrons and photooxidation by valence band holes). In general, photocatalytic processes do not require the use of added oxidants other than dioxygen (already present in the airborne streams). Reactive hydroxyl radicals are produced photolytically on the surface of the catalyst in the presence of water and/or oxygen molecules eliminating the need for addition of activated oxygen containing species. Thus, PEC detoxification is, in principle, less energy intensive than noncatalytic homogeneous photolysis. In addition, the catalytically active surfaces present in PEC systems enhance the photodegradation kinetics and increase the extent of HOC conversion.

Destruction and removal efficiency is a parameter by which the efficacy of any remediation method is assessed. For photocatalytic processes, DRE depends upon the availability of the radiation at wavelengths capable of effecting the target waste compounds. For most nitrate esters, radiation at the middle UV range, wavelengths of 200-300 nanometers (nm), is needed to directly decompose these compounds. The electronic adsorption band for single nitrate chromophor (-ONO₂) is characterized by the molar extinction coefficient of $\epsilon_{max} = 12$ M⁻¹cm⁻¹ (very weak absorption) at the wavelength of $\lambda_{max} = 270$ nm. Figure 1 depicts the UV spectrum of a solution containing 150 ppm 2-hydroxymethyl-2-methyl-1,3-propanediol trinitrate (Trimethylolethane trinitrate, TMETN) in water. The spectrum contains strong absorbance only for wavelengths below 240 nm. The UV spectrum of Figure 1 is typical of all nitrate esters, indicating strong absorbance below 240 nm radiation.

Experimental

We have used two types of photosystems, i.e. photogravimetric analyzer and continuous flow reactors.

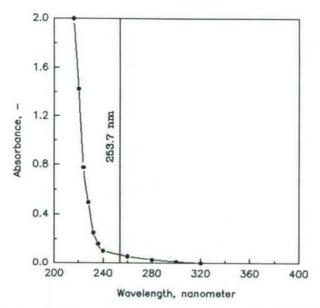


Figure 1. UV spectrum of 150 ppm TMETN in water, scan speed: 500 nm/min (data: courtesy of NSWCIH).

Photogravimetric analyzer

A photogravimetric analyzer (PGA) was fabricated and used to study the kinetics of NG decomposition in presence of different photocatalysts. PGA consisted of a UV light chamber containing 16, 25 W low pressure mercury lamps, a Sartorius the brand, dual range, model R 200 D digital microbalance (utilized in bottom loading configuration), a quartz reaction tube, copper hangdown wire (5 micron OD) and a pyrex glass rod used to support the photocatalyst (12 mm OD & 63 mm length). Titania (Degussa, P25) was immobilized onto the surface of the glass rod (having a loading density of approximately 0.735 mg/cm²). The details of the immobilization technique is given elsewhere (9). In a typical experiment, the catalyst coated cylinder surface was covered with small amounts of pure NG by application of NG/ethanol solution and subsequent drying of the cylinder surface with hot air. The average loading density of NG on the catalyst surface was 0.35 mg/cm².

The NG-coated sample rod was attached to the balance, using a thin copper wire, suspended inside the quartz tube located within the UV light chamber. Air was then passed through the reaction tube at a rate of approximately 54 ml/min. The dynamic weight changes were observed and recorded both prior and after sample irradiation.

Continuous flow photoreactors

Photochemical experiments involving airborne VOCs were conducted in several specially designed and fabricated, continuous flow reactors. In the type A reactor, the light source was placed within the reactor, in direct contact with the reaction media. This configuration

allowed process stream to be radiated internally, making it possible to use Pyrex glass for constructing the reactor tube. Two photoreactors were made according to this configuration, i.e. Mark Ia (0.03m OD, 0.9m length, 327 ml volume) and Mark Ib (0.151m OD, 0.752m length, 12.78 l volume). Mark Ia photoreactor had a large aspect ratio (tube length to diameter) of 30. Mark Ib reactor, having an aspect ratio of 4.91 and a large tube diameter, was also built and tested. Type B photoreactor used a concentric circular tube annulus configuration, with both inner and outer tubes fabricated using fused silica. Mark II reactor was 0.694m long and had a flow area of 15.7 cm² and a total volume of 1025 ml. The UV lamp was placed conveniently within the inner tube, isolated from the reaction media via the quartz window. The main advantage of this design was the ability to control the lamp tube temperature independently from the reactor influent flow rate. Unlike type A designs, in the Mark II reactor, reactants did not come into direct contact with the UV lamp. The disadvantage of type B design is that it is considerably more complicated and costly to build. Mark II reactor also had a small diameter and a relatively large aspect ratio.

No other characteristic differences existed among these reactors other than those mentioned above. All three reactors used identical UV light source and similar techniques were used to introduce reactants into the system. Methods of products collection and analysis as well photocatalyst deposition were also similar for all these systems. In the following, a detailed description of the main components of the Mark II system, representative of all three reactors, is described.

Light source

We used VoltarcTM brand, low-pressure, mercury vapor, hot cathode, ozone-producing germicidal lamps for both photolytic and photocatalytic flow experiments. The construction, filling and operating conditions of the low pressure mercury lamps are such that allow very high efficiency with which electrical input energy is converted into resonance radiation. For a typical hot cathode lamp, about 60% of the power input into the lamp is radiated by the arc as resonance radiation at 185 and 253.7 nm, with about 3% appearing at other wavelengths, mainly in the visible range (10). Figure 2 depicts typical optical output characteristics of the Voltarc lamps used in this work. It can be seen that these UV lamps are sources almost exclusively of 253.7 nm radiation, *i.e.* they contain approximately 92% λ 253.7 nm radiation (at 40°C wall temperature) and 7% λ 184.9 nm radiation (at 43.3°C wall temperature).

The lamp operating temperature has little direct influence on the efficiency of the lamp. However, as the tube temperature increases, more mercury is vaporized and the vapor pressure of Hg increases. If the mercury vapor pressure is too high, self-adsorption reduces the output of resonance radiation as the elastic losses due to electron-Hg atom collisions become significant. The optimum pressure is about $7x10^{-3}$ Torr, which corresponds to a tube temperature of approximately 40° C (10). For Voltarc lamps, the effect of cold spot temperature is given in Figure 3. The curves depict the UV output as the function of lamp tube temperature. A desired spectral output is obtained by manipulating the bulb-wall

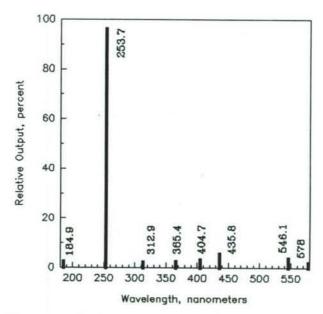


Figure 2. Relative spectral power distribution of VoltarcTM ozone-producing germicidal lamps.

temperature in the range of 40-70°C. The shape of each curve, in Figure 3, is a function of lamp current and the selection of the cold spot temperature. Since the 253.7 nm radiation destroys ozone, the maximum amount of ozone is produced when the cold spot temperature

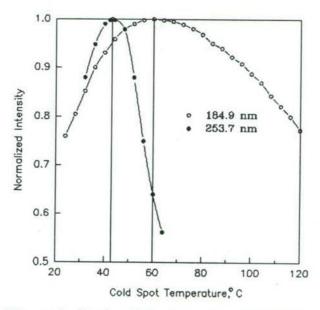


Figure 3. Ratio of the intensity of $\lambda 253.7$ to $\lambda 184.9$ nm radiation vs. temperature (courtesy of VOLTARC TUBES, Inc.).

is approximately 60°C or higher. We made provisions to measure and control the lamp tube temperature in all flow experiments by varying the flow rate of inert gas used to cool lamp cavity, as discussed below. Finally, a Magtrol (model 4612) power analyzer was used in the course of some experiments to directly measure the actual power consumption of the UVlamp. Our measurements indicated that after an initial period (lasting approximately 5 minutes) during which the lamp power consumption peaked, a steady state operation was obtained and the lamp's input power stabilized around 58±1.5 W.

Annulus flow reactor

A schematic diagram of the Mark II system is given in Figure 4. The reactor consisted of two concentric fused silica tubes connected together to form an annulus flow passage. The UV lamp was placed within the inner tube and cooled with a continuous flow of nitrogen or argon gas. A type K thermocouple, placed within the lamp cavity, continuously monitored lamp wall temperature near the coolant outlet port.

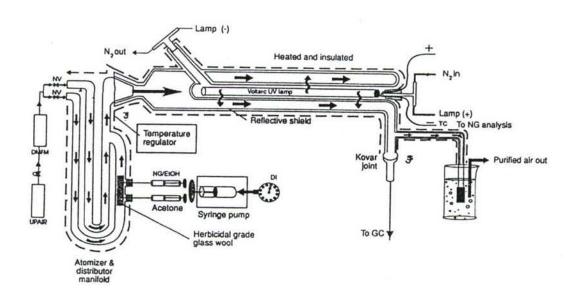


Figure 4. Mark II continuous flow photocatalytic reactor.

Photocatalytic experiments were performed using TiO₂ (Degussa, P25), immobilized onto the inside wall of the outer reaction tube. The entire reactor was wrapped with a highly reflective aluminum foil, heated and insulated. The reactor wall temperature was maintained at a constant 66°C temperature via a type K thermocouple was placed on the outer reactor wall, halfway along the reactor, and a Love Controls microprocessor-based, self-tuning, process temperature controller (model 32110-5150). The reactor exit port consisted of a heated and temperature controlled (at 66°C) tee which attached to two analytical sections, as depicted in Figure 4. All photolyses experiments were performed at

near ambient pressures measured using a Dwyer model 12308WM anemometer and a standard mercury column barometer (Princo brand).

One portion of the reactor effluent stream entered directly into the gas chromatographic (GC) system via a special Kovar borosilicate to metal joint, connecting the reactor to the GC's automatic sample injection port. Also, through a heated glass line, another portion of the flow, exiting the photoreactor at a flow rate of less than 200 ml/min., entered into an ACE Glass sampling bubbler, with #3 fritted stopper, containing a specially prepared adsorbing solution. We also used bubble flow meters to measure air flow rates at reactor outlets. Special care was taken to ensure that the entire process train comprised only of clean Pyrex, fused silica or stainless steel components.

Mixing manifold

We used a specially designed two-passage manifold to meter, mix and airborne VOCs and NG samples. The mixing manifold consisted of a preheater where the temperature of the carrier gas (air, argon or helium/oxygen, etc.) was raised to a desired level, normally around 70-80°C. Also, the entire manifold section was wrapped with a heating element and insulated to allow a uniform mixing temperature (see Figure 4). The manifold temperature was monitored, controlled and maintained at a constant 66°C level by means of a type K thermocouple, placed on the glass wall near the sample injection ports, and the use of another Love Controls PID process temperature controller. For reasons of safety and repeatability, we took much care in selecting materials of construction, design and fabrication of the photocatalytic system. Provisions were also made to ensure uniform and thorough heating of the entire process train to prevent unwanted NG condensation, adsorption and/or concentration along the process lines. Efforts were made to adhere to the accepted safety guidelines provided by our contracting agency (NSWCIH) for the handling and use of energetic compounds, in general, and nitroglycerine, in particular. For example, all the surfaces and process lines that came into contact with the NG vapor were smooth and heated surfaces made out of mostly glass or fused silica with minimal sharp turns, corners, wedges, etc. After each photolytic experiment, all the collection vessels were disassembled and washed using special solvents. A detailed material balance of all the reactants and products was carried out after each experimental run.

Spirits of 10% NG in ethanol were shipped from NSWCIH in small 500 ml bottles. At FSEC, we prepared several milliliter sample of NG/ethanol/acetone solution by blending a known quantity of NSWCIH spirit with food grade ethanol obtained from the Florida Distillers Company at Lake Alfred, FL and Fisher Scientific brand, HPLC grade acetone (99+%). The volumetric and gravimetric composition of the blend were determined and found to be NG:ethanol:acetone = 2.3:59.9:37.8 percent by volume and 4.50:58.56:36.94% by weight, respectively. In a typical experiment, using a 25 microliter syringe (Scientific Glass Engineering, 300 series Analytical Syringe), a known volume of reagents from the prepared NG/ethanol/acetone solution was injected into the reactor. The reagents were introduced into the mixing manifold using a SAGE, model 341B syringe pump, recalibrated

in our Laboratory. The pump was modified to allow both a dual syringe operation, if needed, as well as ability to measure the precise volume and rate of sample injection into the photoreactor, directly. This was done by incorporating a linear motion dial indicator (Teclock model AI-951D), accurate to 0.001". The reagents were introduced into the heated manifold through a special high-temperature septum at a preset and steady injection rate of 1.475x10⁻⁶ l/min. At injection point, the manifold was packed with glass wool (herbicidal-grade) to allow high surface area and facilitate rapid evaporation of the reagents. The carrier gas entered through two separate lines, *i.e.* injection port line and bypass port line. Each flow line was heated to a constant temperature of approximately 70°C and metered, independently, using two HFM-200 series Teledyne Hastings Raydist mass flow controllers.

Analytical methods

Analyses of reactant concentrations were performed using both gas chromatographic and spectrophotometric techniques. The gas chromatographic system consisted of a Varian GC 3400 equipped with flame ionization and thermal conductivity detectors. The sample introduction into the GC took place at a desired time by injection via a 1 ml sample loop and the automatic sample injection port. The gas chromatographic system was configured in a manner to allow simultaneous analyses of the permanent gases (i.e. O2, N2, CO, CO2, CH4, and HCs) as well as ethanol, acetone, and other compounds and potential by-products of the photolytic reactions (i.e. aldehydes, organic acids, etc.) can be accomplished. We used two 1/8" packed columns, one 6' and the other 30' long, HayeSep DB (high purity divinylbenzene) polymer, 100/120 mesh packing (Hayes Separation, Inc.). The 30' column was placed outside the GC at ambient temperature and used to separate light molecular weight gases (H2, O2, N2, Ar, CO, NO and CH4). The 6' column was placed within the GC oven and temperature programmed to allow the separation and analysis of all the remaining compounds of interest. An automatic 4-port valve (VICI) provided the capability to switch between the two packed columns. We also used a second 4-port valve (VICI) to switch on and off a special Ni catalyst, used to methanize CO and CO₂ for analyses by the FID detector. Several standard gas mixtures containing H2, O2, N2, Ar, CO, CO2, CH4, C2H6, C₂H₄, NO, N₂O and NO₂ at various concentrations and compositions (obtained from the Air Products and Chemicals and Liquid Carbonics) were routinely used to calibrate the GC response. We also obtained high purity HPLC grade acetaldehyde, acetic acid (Aldrich brand) and acetone (Fisher brand) and used for the purpose of GC analysis and calibration. The ethanol standard was food grade as described above.

The quantitative analysis of NO₂ and NG, however, posed the most difficult challenge as we expected detectabilities well below 1 ppm for these compounds. Spectrophotometric system consisted of a 1 kW xenon light source with quartz optic primary condensing system, providing a broad band continuous radiation from 250-1150 nm. Also, the system was equipped with a Spectral Energy GM 252-40 monochromator having 500 nm blaze grating, GMA 2560 quartz entrance prism, and forward and rear quartz focussing sleeves. A GMA 301-4 stepper motor and control was also employed to enable continuous or repetitive wavelength scanning with analog output. An Oriel #77348 photomultiplier tube held in a

mountable, side-on housing, with Oriel #7070 power supply and digital readout, provided the light detection capability. A number of neutral density, infrared, and ultraviolet filters, as well as an infrared-absorbing water filter with quartz windows, assembled in-house were used, as needed.

A spectrophotometric technique for the simultaneous analysis of NG and NO2 was developed in our Laboratory. The technique was employed for the analysis of NG in either aqueous or gaseous media. In this method, the reactor effluent was passed through a bubbler which contained a special absorbing solution that formed an intense pink color in the presence of hydrogen peroxide, sulfanilamide and others. The optical density of the solution was determined spectrophotometrically. Quantitative measurements indicated that the amount of NG in the absorbing solution corresponds, stoichiometrically, to that of nitrite ions present which form intensely colored diazosulfanilamide according to the following reaction:

$$R-NH_2 + NO_2^- + H_2O_2 - R-NH-N = O - R-(OH)N_2$$
, where $R - C_6H_4SO_2NH_2$.

Analysis of NO2 concentrations were also performed spectrophotometrically, according to an EPA Protocol (11). Calibration curves depicting the photocurrent vs NG concentration were constructed which allowed NG analyses in the samples to be performed in concentration ranges well below 0.1 ppmv. The modification of these methods have made simultaneous analysis of NG and NO2 in the gaseous samples possible (12).

Results and Discussion

A large number of experimental runs were carried out in both type A and type B Experiments included both photolytic (UV only) and photocatalytic photoreactors. (UV+TiO2) trials. In some experiments only acetone and ethanol were introduced into the In others, airborne VOCs (ethanol+acetone) also included predetermined quantities of nitroglycerine. We used both synthetic (oxygen+nitrogen only) and simulated (O₂+Ar or O₂+He) air as the carrier gas for the organic vapors. Air flow rates varied in a wide range, i.e. 0.1-24 l/min. The concentration of NG in the air was also varied widely, i.e. from 9 to 74 ppmv. The reactor temperature was maintained in a range of 70-100°C. In a typical experiment, the composition of NG, acetone and ethanol in the air entering the photoreactor was 14, 450 and 900 ppmv, respectively. Most light experiments (with or without TiO2 present) preceded by dark runs (no UV present) under identical experimental conditions. No reaction was observed in the reactor under all experimental conditions with no radiation (dark reactions) and with or without TiO2 photocatalyst present. A summary of the findings for both the photolytic (no TiO2 present) and photocatalytic (with TiO2) is given below.

Photolytic (homogeneous) decompositions

Chromatographic data of Figures 5-7 indicate that, photolysis (no TiO₂ present) only partially mineralizes gas-phase VOCs present in synthetic (oxygen+nitrogen) and simulated (oxygen+argon) air as well as pure helium at flow residence times as high as 4 min. Main reaction products of acetone-ethanol photodecomposition in the presence of oxygen were carbon oxides. While, in the absence of oxygen, the conversion was incomplete (especially with respect to acetone) and the product slate also included light hydrocarbons, acetaldehyde, acetic acid and traces of some other unidentified compounds. It should be noted that, although the reaction train was heated everywhere to maintain a constant wall temperature of 66°C and prevent undesirable condensation of the NG, no reactions took place under no-light conditions as indicated by the data of Figures 5-7. The rationale for using simulated air (argon+oxygen) and helium carrier gases was that the nitrogen contained in air made it extremely difficult to chromatographically determine if any N₂ was produced as a result of NG photolysis in the reactor.

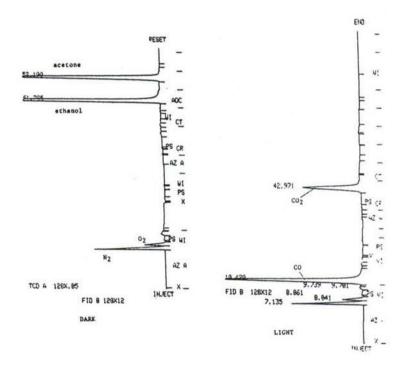


Figure 5. Non-catalytic photodecomposition products of acetone-ethanol (1770 & 5000 ppmv) in synthetic air (oxygen+nitrogen), Mark II photoreactor, residence time = 4 min., dark and light experiments.

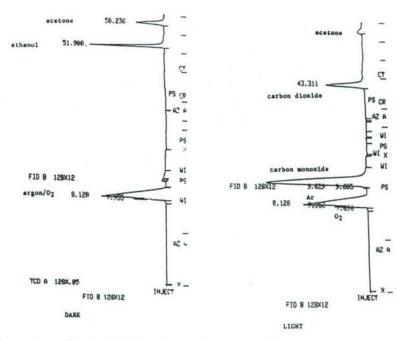


Figure 6. Non-catalytic photodecomposition products of NG-acetone-ethanol in simulated air (oxygen+argon), Mark II photoreactor, residence time = 3.82 min., dark and light experiments.

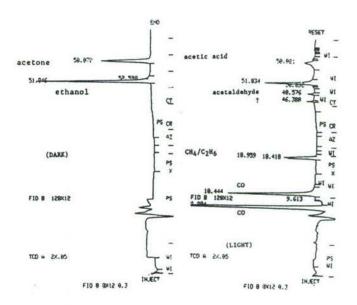


Figure 7. Non-catalytic photodecomposition products of NG-acetone-ethanol in pure helium, Mark II photoreactor, residence time = 4 min., dark and light experiments.

Results, to date, indicate that under certain experimental conditions, photolysis of NG (no TiO₂ present) resulted in its almost quantitative decomposition. Figure 8 depicts the extent of NG decomposition and the NO₂ yield as a function of the flow residence time in the photoreactor. At a residence time of 100 s, a DRE of about 99.1% was obtained for the NG in the reactor. Also, the concentration of NG in the effluent stream was only 0.13 ppmv. At higher flow rates, the DREs for NG decomposition dropped drastically and at a residence time 7.2 s, the concentration of NG in the exit gas reached 3.05 ppmv. The NO₂ yield, produced as a result of NG decomposition, was found to vary with the residence time of the flow in the reactor, higher at the low residence times. It was found that the DREs for NG photolysis using low-pressure mercury lamps was quite high even at relatively high NG concentrations. For example, photolysis of air containing 74 ppmv of NG at a flow rate of 0.2 l/min., in the absence of titania, gave a DRE in excess of 99.86% and the concentration of NG in the effluent stream was found to be less than 0.1 ppmv.

Photocatalytic (heterogeneous) decompositions

Chromatographic data of Figure 9 depict typical results obtained from photocatalytic decomposition of airborne acetone-ethanol in the Mark II photoreactor. This experiment was conducted under conditions similar to that depicted by Figure 5 with only difference being the presence of titania photocatalyst. It can be seen that the mixture of airborne ethanol and acetone was completely mineralized to CO₂ and H₂O with no apparent traces of CO detectable.

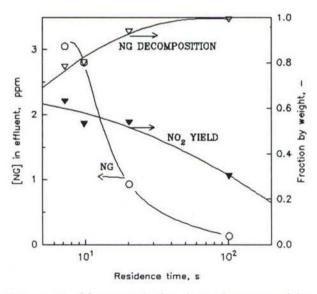


Figure 8. Non-catalytic photodecomposition of NG in Mark Ia reactor, [NG]_{in} = 13.7 ppmv.

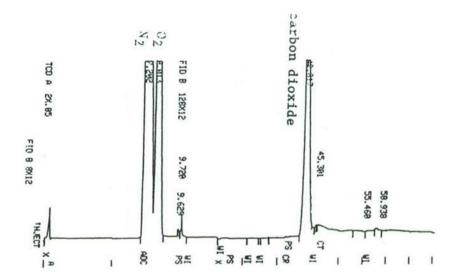


Figure 9. Photocatalytic decomposition products of the acetone-ethanol decomposition in synthetic air (oxygen+nitrogen), Mark II photoreactor, TiO₂ loading = 0.12 mg/cm², residence time = 7.1 min.

In an attempt to determine if appreciable amounts of nitrogen, nitrous or nitric oxides were generated as a result of NG photodecomposition in the reactor, few experiments were performed using simulated air (oxygen+helium) as the carrier gas. The rationale for using simulated air was that nitrogen contained in air makes GC analysis of N₂, N₂O and NO (from low concentration NG photolysis in the reactor) very difficult. Furthermore, these compounds produced no spectrophotometric signature and therefore could not be analyzed using the methods developed for NG and NO₂ determination. Typical results are given in Figure 10 indicating an almost complete conversion of acetone-ethanol to carbon dioxide and water with minute traces of CO, ethane, acetaldehyde, and unconverted acetone and ethanol. The small nitrogen peak present is apparently a contamination in the flow system and not necessarily resulted from NG decomposition. This small nitrogen peak was observed in injections during the dark period before the lamp was turned on. Anyhow, chromatographic results obtained, to date, are inconclusive for us to draw a firm conclusion as to the extent of the N₂, N₂O and NO formation resulting from photocatalytic decomposition of NG.

Figure 11 depicts typical photocatalytic NG decomposition results, obtained in the Mark Ia reactor. The data indicate that in the presence of TiO₂, immobilized directly onto inner surface of the photoreactor, DREs for NG decomposition are high, even at the gas residence times down as low as 10 s. In comparison with photolytic decomposition data

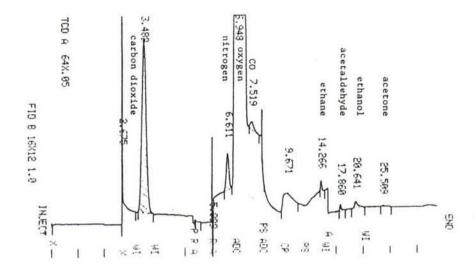


Figure 10. Photocatalytic decomposition products of NG-acetone-ethanol in simulated air (oxygen+helium), Mark II photoreactor, residence time = 4 min., $[NG]_{in} = 30 \text{ ppmv } \& [NG]_{out} = 0.2 \text{ ppmv}$.

obtained under similar conditions, the residence time needed to decompose nitroglycerine, with destruction and removal efficiency of 99%, per se, would be about 10 times shorter for a photocatalytic system.

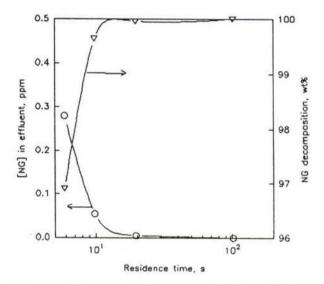


Figure 11. Photocatalytic (TiO_2) decomposition of NG in Mark Ia reactor, $[NG]_{in} = 13.3$ ppmv.



Results obtained from photocatalytic NG decomposition experiments conducted in inert argon atmosphere provided an interesting finding. It was found that the presence of air is not critical and the photocatalytic NG decomposition rates are sufficiently high even in absence of strong oxidizers such as ozone, although in air streams, DRE for NG is highest, indeed. For example, at a residence time of 12 s, the NG decomposition in Ar exceeds 99.5 wt%, while NG concentration drops from initial 18.6 ppmv to 0.1 ppmv at the reactor output.

Photocatalytic experiments performed at higher NG concentrations indicated high DREs for NG decomposition in air. For example, introducing a gaseous mixture containing 72.2 ppmv of NG into the photocatalytic reactor resulted in a DRE equal to 99.94% for NG destruction in air at a flow rate of 0.2 l/min.

The comparison between two types of photocatalytic reactors used, i.e. Mark Ia and Mark II, indicated no appreciable difference in the NG destruction and removal efficiencies, at least in the range of flow rates not exceeding 0.5 l/min. Thus, the quartz window used in the Mark II reactor does not affect the overall efficiency of the photocatalytic decomposition process.

A series of experiments was also conducted in the Mark Ib reactor in order to study the effects due to the increased reactor throughputs. Figure 12 depicts the representative data for the photocatalytic decomposition of NG in the Mark Ib reactor. Mark Ib system was a specially designed photocatalytic reactor having a relatively large volume (12.8 l). Our experimental findings indicated that it was possible to increase the air flow rates well beyond 20 l/min without an appreciable drop in the NG decomposition rates, using the same amount of power. For example, at a flow rates of 10 l/min., the DRE for NG decomposition was found to be 99.7% and the concentration of NG in the effluent of the reactor dropped from 11.3 ppmv to a level below 0.1 ppmv. Considering a lamp power input of 57 W, the process energy requirement would only be about 163 W/SCFM of reactor input flow.

Finally, a series of experiments was conducted to explore the possibility of photocatalytic decomposition of NG (no catalyst present) and to obtain preliminary information about efficiency of various photocatalysts. Studies involving the kinetics and mechanisms of condensed-phase reactions are best carried out using thermogravimetric analyzers. We used a specially designed photogravimetric system to study photocatalytic decomposition of pure NG deposits on the surface of different materials (i.e. TiO₂, ZnO, Al₂O₃ and SiO₂). An average catalyst loading density of 0.7 mg/cm² was employed for most photogravimetric experiments. When the light was turned on, the weight of the glass rod used to support the NG-coated catalyst dropped, but only in the case of TiO₂ (Degussa, P25) that NG decomposition proceeded to completion (see Figure 13). Examination of the surface of TiO₂ showed no traces of polymeric or carbon deposits.

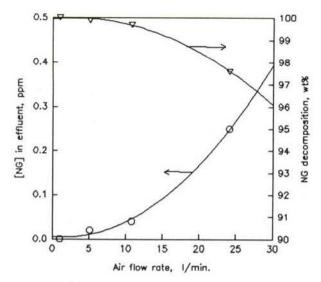


Figure 12. Photocatalytic (TiO_2) decomposition of NG in Mark Ib reactor, $[NG]_{in} = 12.2$ ppmv.

Mechanism of NG decomposition

Kinetic curves of NG decomposition apparently are not consistent with a simple first-order reaction scheme. A non-exponential dependence, especially in the case of photocatalytic NG decomposition, indicates the possibility many different reaction pathways open to NG. Thus, NG decomposition reactions include both photolytic (homogeneous), *i.e.*

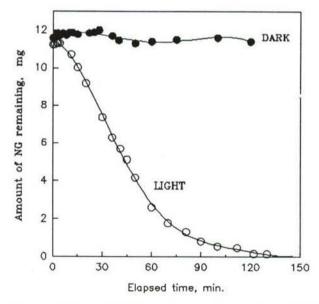


Figure 13. PGA curve for the NG photodecomposition on TiO₂.



NG +
$$hv \rightarrow \text{products}$$

NG + O_2 + $hv \rightarrow \text{products}$
NG + O_3 (dark) $\rightarrow \text{products}$

as well as photocatalytic (heterogeneous), i.e.

NG + TiO₂ +
$$hv \rightarrow products$$

NG + TiO₂ + O₂ + $hv \rightarrow products$
NG + TiO₂ + H₂O + $hv \rightarrow products$
NG + TiO₂ \rightarrow (NG)_{ads.}/TiO₂
(NG)_{ads.} + $hv \rightarrow products$

reactions.

First step involving photolytic NG decomposition is, most probably, the rupture of $CO-NO_2$ bond, which is the weakest bond in the molecule ($E_b = 36.4 \text{ kcal/mole}$), yielding nitrogen dioxide NO_2 , and a highly reactive radical that will be immediately decomposed.

In the presence of the photocatalyst, NG reacts with the active species, photogenerated on the surface of TiO₂, i.e.

$$TiO_2 + hv \rightarrow TiO_2(e^-) + TiO_2(h^+)$$

$$TiO_2(e^-) + NG \rightarrow products$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2(O_2^-)_{ads.}$$

$$TiO_2(O_2^-)_{abs.} + NG \rightarrow products$$

$$TiO_2(h^+) + NG \rightarrow products$$

$$TiO_2(h^+) + OH \rightarrow TiO_2(OH)_{ads.}$$

$$TiO_2(OH)_{ads.} + NG \rightarrow products \dots etc.$$

At this point additional experimental data are required before one can mark out one or several routes as the most viable for the NG decomposition. In all likelihood, in a practical photocatalytic process, all of the reactions above would contribute, but to a varying degree.

Conclusions

Our findings, to date, indicate the viability of a titania-based, UV-driven photocatalytic oxidation system for rapid, efficient and cost effective destruction of airborne VOCs containing acetone, ethanol and nitroglycerine vapors. It was shown that an effective photocatalytic reactor can be very simply and cost effectively assembled from readily available, environmentally acceptable materials. The use of TiO₂ poses no special difficulty as it is used widely in a large number of consumer products, including some toothpastes. The use of photocatalytic method eliminates the need for using very expensive and sophisticated UV light sources (pulse xenon arc lamp) and/or added active oxidants (e.g. H₂O₂, O₃, etc.) for photodecomposition of airborne organic and energetic compounds. Although the system described here is yet to be fully optimized, nevertheless, findings to date indicate a reasonable process energy requirement of about 163 W/SCFM of reactor flow. The photocatalytic system described here does not require any exhaustible reagents or materials and does not produce any toxic by-products as a result of its operation. The system can be made mobile and can operate anywhere that AC power. The process, by its nature, can readily be scaled up for a given application.

The future work will involve more complete product analysis (especially very low levels of N_2 , N_2O and NO), and further mechanistic studies. We note that the main goal of this work has been the development of a cost effective UV photocatalytic oxidation system for the treatment of air, contaminated with nitroglycerine and other volatile organic compounds. Now, it appears that the next logical step is to upscale the process from liter per minute capacity to a pilot-scale demonstration.

Finally, the results of this work is being employed, presently, in development of a solardriven, photocatalytic system for the treatment of NG-contaminated waste streams. To date, a prototype flat-plate solar detox unit has been built and successfully tested. The unit is being evaluated for its effectiveness in removing and mineralizing dilute organic wastes.

Acknowledgments

The authors wish to thank Drs. David Block, Kirk Collier, and Clovis Linkous of the Florida Solar Energy Center for their contribution to this project. We also thank Mr. Najib Abdulsamad (FSEC) for providing valuable engineering support for the entire effort. This work has been sponsored by the U.S. Department of Navy, Naval Surface Warfare Center, Indian Head Division, Maryland, and the United States Army, Production Base Modernization Activity, Picatinny Arsenal, New Jersey, under contract No. N00174-91-C-0161. We thank Dr. Chester Clark, and Messrs. Ed Garcia and Chuck Painter (all with NSWCIHD), and Robert Goldberg (PBMA) and Ms. Florence Elie (PBMA) for their support of this work.

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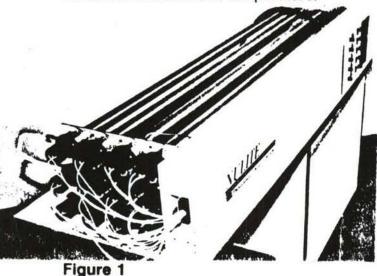
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16th Annual Army Environmental R & D Symposium

Novel and Cost Effective Treatment of Air or Water Contaminated with Hazardous Organics Using TiO₂ Photocatalytic Treatment Systems

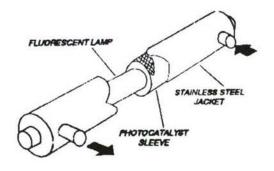
Presented By - Brian Butters

General Manager, Nutech Environmental 511 McCormick Boulevard London, Ontario N5W 4C8 (519) 457-2963 Titanium Dioxide (TiO₂) photocatalytic systems as shown in Figure 1 are used to efficiently remove and destroy organic contaminates from air or water in a solid state, continuous flow process which occurs at the ambient temperature.



The TiO₂ photocatalytic destruction process was first discovered in 1976. The process remained a laboratory curiosity until 1986 when work began in earnest to develop fieldable systems based on this discovery. Since that time, various

research efforts have concentrated on fixed or slurry TiO₂ which is electrically or solar powered.



The photocatalytic treatment systems discussed in this paper are based on TiO₂ fixed to a porous matrix wrapped around a fluorescent light source; as developed by Nutech. The major advantage of this system is that it can be used to treat both air and/or water contaminated with organic pollutants.

When the TiO₂ semiconductor material is stimulated by UVA light, it produces radicals such as hydroxyl radicals, which break the carbon bonds of hazardous compounds.

This process, when given sufficient time, will reduce most organics (carbon based compounds such as PCB, phenols, dioxins, and BTEX) to carbon dioxide and water.

It should be noted that only UVA light is used in these systems, as the shorter wave length UV light can complicate the level of detoxification and inhibit the rate of reduction of Total Organic Carbon (TOC).

The electromagnetic radiation spectrum

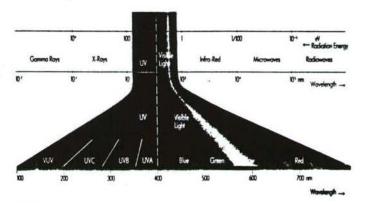


Figure 3

Figure 2



PERFORMANCE

System performance means different things to different people. In this paper, performance refers to such measures as rates of destruction, or rates of TOC removal (which is a greater level of work than simply destroying an identified compound), system life, capacity, direct operating cost per volume treated, electrical efficiency and quantum efficiency.

Figures 4 & 5 show unoptimized treatment rates for organic compounds at various concentrations in a variety of actual water samples.

Typically, destruction is achieved in periods of 30 seconds up to a few minutes and TOC removal is also in the range of 30 seconds up to **nominally** 30 minutes. Again, this depends on treatment requirements and types of contaminants.

At high concentrations of organics or when dealing with more refractive contaminants, certain additives such as hydrogen peroxide can be added in small quantities (0.003 mole per litre) to accelerate the reactions. These additives function by inhibiting the electron hole recombination process as depicted in Figure 6.

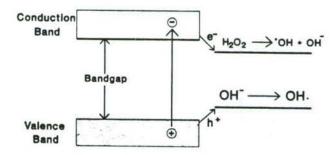


Figure 6

By this process, quantum efficiencies as high as 70% have been achieved and increased in rates of reaction by 1 to 6 times.

Typical system sizes at the current level of development are:

TYPICAL TREATMENT SYSTEM PARAMETERS
(At Current Level Of Development)

Dwell Time (min)	Capacity US GPM	# of Wafers	Volume (ft³)	Power (kW)
1	5	9	44	10
1	25	27	132	31
4	5	37	180	42
4	25	111	541	126
2 sec	150 (cfm)	9	28	9

It should be noted that the treatment rates, power requirements and equipment size stated today are based on the current level of development and reflects a doubling of efficiency over the past 12 months. On-going work in reactor design, power supplies, lamp development and catalyst will show comparable gains over the next 12 months.

Figure 4

VARIOUS WATER AND AIR FIELD SAMPLES *

Contaminant	Conc Initial	entration ——>	Final	Rate	Power Cost (\$0.05/kWh)
SAMPLE - St.	Lawrence R	liver wate	r		
THM TOC Colour	930 ppb 6.1 ppm 37	>		626.6 ppb/min 4.7 ppm/min	\$0.52/1000 gal.
	lp & paper I C-stage+1/3 037 mol/L of	3 E-stage	turbid solut	rbid, tion	Garage Care
TOC COD BOD AOX	375 ppm 850 ppm 290 ppm 52 ppm	<u> </u>	200 ppm 20 ppm	10 ppm/min 21.7 ppm/min 9 ppm/min 1.1 ppm/min	\$14.25/1000 gal.
SAMPLES - Water misc.					
2,4 DCP 2,4 DCP	40 ppm 200 ppm		29 ppm 183 ppm	11 ppm/min 16.8 ppm/min	\$0.63/1000 gal. \$0.63/1000 gal.
SAMPLE - CV	OC in Amb	ient air			
TCE TeCE TCE	17893 ppm 4630 ppm 30 ppm	>		2299 ppm/sec 595 ppm/sec 36 ppm/sec	\$0.07/hr - 1 cfm \$0.07/hr - 1 cfm \$0.50/hr - 75 cfm

^{*} At Current Level Of Development



BTEX FIELD SAMPLES *

Contaminant Concentration Rate **Power Cost** Initial ---> Final (\$0.05/kWh) SAMPLE - BTEX contaminated ground water from gas station site with 80 ppm carbonate, silt and iron (no pretreatment) Benzene 9 ppm ——> 5.2 ppm ----> 4 ppm Toluene 7.2 ppm $0.53 \text{ ppm} \longrightarrow 0.25$ Ethybenzene 5.9 ppm ——> 2.63 ppm 22.63 ppm ——> 12.08 ppm **Xylenes** TOTALS 7 ppm/min \$0.95/1000 gal. SAMPLE - BTEX contaminated ground water from gas station site - 80 ppm carbonate removed, and .003 m/litre H₂O₂ added Benzene 6.8 ppm ——> 0.01 ppm ----> 0.005 ppm Toluene 5.9 ppm 0.43 ppm ---> 0.5 ppb Ethybenzene ----> 3.4 ppb **Xylenes** 4.1 ppm 17.23 ppm —> 0.018 ppm TOTALS 11.5 ppm/min \$0.95/1000 gal. SAMPLE - BTEX contaminated drinking water from a residential well - 250 ppm carbonate removed Benzene 380 ppb ——> 2.6 ppb Toluene ----> 0.2 ppb 31 ppb Di-isoproyl ether 100 ppb ——> 5 ppb TOTAL ----> 7.8 ppb 521 ppb 342 ppb/min \$1.80/1000 gal.

^{*}At Current Level Of Development

Another important aspect of the technology is the useful life and maintenance requirements of the components which make up the systems. From the component performance discussed below, it is expected that the systems will be robust and will require minimal attention when in service.

- Lamp

No lamp has yet to fail in service. The lamps have demonstrated a 4000 hr life to date and one year lamp life is anticipated in most applications

Ballast

Expect multi year life consistent with conventional applications.

- Catalyst

No catalyst failure of any type since introduction in 1989. Mesh endurance testing has exceeded 2200 hours and continues. The problem of metal cation fouling has been solved, and the electron recombination process has been significantly inhibited. There is no problem with biological fouling and in fact, the catalyst eats the ink labels off the lamp.

Currently, there are ten demonstration systems in the field, three of which are air, and all but one are in the private sector. All systems have met or exceeded their performance requirements. Systems continue to be fielded at the rate of at least one per month.

SYSTEM BENEFITS

The major benefits of this technology are:

- SOLID STATE
 - reliable, minimal maintenance
- NO NOISE, LOW PROFILE
 - ergonomically acceptable
- DESTRUCTIVE
 - reduces liability and disposal cost
- ENERGY EFFICIENT
 - low direct operating cost
- NO BIOLOGICAL FOULING
 - non issue
- CONSISTENT PERFORMANCE

Additional benefits of this technology are:

- systems constructed from off the shelf components
- systems not influenced by turbidity
- modular installation in 1 gpm capacities
- variable flow rate to handle swings in contamination levels
- system able to operate over a wide pressure range and pressure drops.
- will operate over a wide range of temperatures
- will operate over a range of pH
- instant on/off capability
- Basic service skills only
- capital cost comparable to established technologies
- working fluid requires no or minimal pretreatment

APPLICATIONS

Typical water application for TiO₂ Photocatalytic treatment system include:

- The manufacture of Ultra Pure Water to reduce TOC to levels below 1 ppb.
- The detoxification of drinking water



- The detoxification or purification of plant process water of organics prior to discharge or reuse.
- The removal and destruction of hazardous organics in groundwater

Similarly TiO₂ Photocatalytic air remediation system can be used to remediate:

Air emissions from air strippers, vapour extraction system or steam stripping and other water remediation process

Air from manufacturing operations where CFC, blowing agent, odours and paint fumes are emitted.

Figure 7 shows a comparison of a typical vapour extraction installation. One using Carbon and the other using a TiO₂ photocatalytic treatment system.

Note the reduction in system complexity when Photocatalysis is used. No moisture separator is required nor is a waste water treatment plant required as the TiO₂ technology functions regardless of moisture content. In addition, the pump power is reduced due to a lower pump head requirement. When using TiO₂ systems there is no disposal requirement for accumulated organics as with GAC which should also be factored in when considering system complexity and cost.

Figure 8 shows a typical water treatment application for groundwater at a plant site. This application could just as easily be for a drinking water supply.

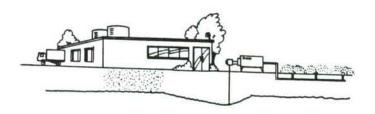


Figure 8

GETTING STARTED

To get started in the use of this system one must first conduct a treatability test to determine the retention time. This may be as simple as treating a 5 gallon (20 litre) sample or the installation of a field trial unit for a brief period of time. Once the retention or dwell time has been accurately assessed, system size and performance can be accurately determined and suitable systems built.

Meanwhile, in the laboratories of Michigan Technological University (MTU), four prongs of work were being explored. The first was a goal to find a more photoactive catalyst than titanium dioxide (TiO2). The approach included platinizing the TiO2, looking at new formulations (SrTiO3 & NiO-SrTiO3), and ways to enhance photoactivity. The second prong was to evaluate the perovskite materials to utilize the lattice oxygen for the oxidation step and was found unsuccessful and not further pursued. The third prong is an adsorption/regeneration process (now called the HAND*D process) using a fixed photocatalyst to destroy the contaminants in the adsorption vessel as they are desorbed. Finally, since most ozone reactions are mass transfer restricted, the last prong focused on the development of an efficient ozonation reactor.

Completing the technology base for the Air Force are three more projects. The first two are Small Business Innovative Research (SBIR) efforts. The technologies developed by the SBIRs (both Phase I's are completed, Phase II efforts are pending) are a photocatalytic film and an electrochemical method for producing ozone. The third project is a joint Air Force/Department of Energy (AF/DoE) effort with the National Renewable Energy Laboratory (NREL, formerly the Solar Energy Research Institute, SERI) in a field demonstration of a titanium dioxide slurry process using a new photoreactor developed for NREL by the University of Florida (UF).

PROGRESS TO DATE

The work at SRI International is near completion, with the final report (REF 1) expected by the end of June 1992. The main results from this effort relate to the oxidant identification and the intercomparison of efficient generation and use of the dominant oxidant. Figure 1 shows the reactivity ratio for the two surrogate species, the propionate and butyrate ions. All of the processes have essentially the same slope, the slope that has been shown for the hydroxyl radical (OH*) formation. Thus each of the processes uses the

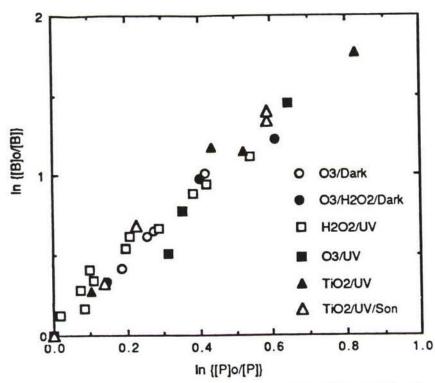


FIGURE 1 Reactivity ratio plot for propionate and butyrate ions in different oxidation systems at pH 7.



OH* as the main oxidant. Comparing, then, what it costs for each of the systems gives the optimum system (or the most destruction for the buck) among the AOPs shown above. The preliminary results were outlined in a recent presentation (REF 2) and are as follows: 1) Drs Mill and Yao found that the most efficient system for generating HO* is the H2O2/UV system (however, this AOP is too slow to use with high flow systems where short residence times require high rates of HO* generation); 2) Ozone AOPs use 250 nm UV light very efficiently, but only 5 percent of the photolyzed ozone forms HO* (this means that only above pH 7 where the HO2- ion is available, the ozone AOP is an efficient source of HO*); and, 3) above pH 7 the ozone/UV AOP has no advantage over O3/H2O2/Dark for generating HO* and oxidizing organics.

The researchers at MTU found (REF 3) that not all TiO2 is the same. This is not in reference to the form of the TiO2 (it comes in three crystalline forms, anatase being the most photoactive). What they found was that when they platinized the anatase TiO2 from the Aldrich Company, the DeGussa Company, and their own formulation, each had different activity for different contaminants. For example, for trichloroethylene (TCE), it was observed that platinized Degussa TiO2 and platinized MTU TiO2 were less active than the respective parent TiO2. However, the Aldrich-platinized TiO2 is five times faster at destroying the TCE over unplatinized Aldrich TiO2. The platinized MTU catalyst was the superior photocatalyst for salicylic acid and 2,4-dichlorophenol destruction. It was observed during the TCE screening tests that SrTiO3 and 1.5% (weight percent) NiO-SrTiO3 catalysts were not photoactive and were not tested any further with other compounds. Work continues in the area of photocatalyst enhancement.

A related effort at MTU is working on concentrating the organics prior to destruction. Kinetics of destruction (and economics) favor treating concentrated waste streams. Unfortunately pump-and-treat technologies produce dilute waste streams that only become more dilute with age. Thus the HAND*D concept was born. Combining a superior photocatalyst with a new highly adsorbant material made by Rohm & Haas (Ambersorb 563) has the potential of being the top contender in the field demonstrations being planned. Work is on-going to determine what classes of contaminants (and in what concentrations) can be loaded onto the modified Ambersorb material, reactor design, and performance of the HAND*D process in the air phase. One reactor prototype is in construction for use in solar applications. The process adsorbs continuously and desorbs/destroys the contaminants during the day. Initial "roof top" tests at Michigan Tech will be conducted during the summer of 1992.

The final prong of work at MTU, the ozonation reactor, is being developed and modelled for oxidation of several contaminants of interest to DoD. The technology may ultimately combine ozone, UV, and TiO2 in the reaction vessel. Air stripping of the contaminants by ozone is minimized by the reduced amount of ozone needed for destruction of the organics in the liquid phase. A ten gallon per minute system is being constructed to be used in conjunction with the SBIR to develop ozone electrochemically. UV enhancement from solar radiation will also be evaluated.

During the six month Phase I effort, Lynntech Inc. demonstrated an electrochemical cell that maintained constant ozone production for 1500 hours (Ref 4). Preliminary economics show that compared to a corona discharge system that the electrochemical process is almost 1/2 the cost to treat contaminated water. Using the advanced ozonation reactor from MTU will only

enhance this system further, thus not only generating ozone cheaper, but utilizing it more efficiently as well. Phase II of the program is in negotiation at this time.

INRAD Inc, the other SBIR, has demonstrated (REF 5) a photocatalyst membrane systems that destroys the organics in a continuous process. The contaminated water flows through a porous membrane which is illuminated by light. The membrane is made up of two components that are fixed to a porous glass support. The membranes demonstrated a six-fold increase in mineralization of benzene and TCE over current slurry photocatalyst technologies.

The last technology work being conducted under the LPC program is the joint NREL/AF effort. A field demonstration of the process is on-going at Tyndall AFB FL at a fuel contamination site (see Figure 2). Monitoring wells in hot zones at the site indicate over 4' of free product floating on the surface of the water table. This will be removed separately, and the contaminated groundwater under the fuel layer will be treated aboveground. Batch runs of the system are used to evaluate the performance of the new reactor design developed by UF. The reactors are based on inexpensive

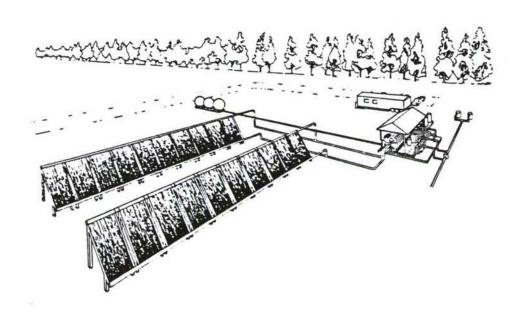


FIGURE 2. ARTIST'S CONCEPTION OF SOLAR DETOX UNIT BEING DEMONSTRATED AT TYNDALL AFB FL (REF 6)

non-concentrating flat plates rather than expensive collector troughs that concentrate the sunlight onto a glass tube carrying the organic contaminated water/photocatalyst slurry. The two month effort is scheduled to be completed in mid-August 1992.

PLANNED EFFORTS

In FY93 an effort is planned to bring forth the best of the treatment units from the technology base developed to date and test them on contaminated

groundwater. The technologies chosen would come from the AOPs (commercially available units), the MTU efforts, the SBIRs, and the joint NREL/AF project. All of the processes would be run simultaneously at one site for six months. Preliminary evaluation of the data would be made and successful processes would be moved to a second site for continued testing for another six months. The contamination sites will be fuel only, solvent only, or a mix between the two. In addition the Phase II SBIR efforts will include field demonstrations of the processes at contaminated sites.

ACKNOWLEDGEMENTS

In this LPC program I am only the conductor. I wish to give credit, and thanks, to the following individuals for their contributions to this vital Air Force program:

Drs Ted Mill and David Yao, SRI International, Menlo Park CA
Drs John Crittenden, David Hand, and Mike Mullins, MTU, Houghton MI
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Dr Oliver Murphy, Lynntech Inc., Bryan TX (ozone generator SBIR)
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Drs Yogi Goswami and Jim Klausner, UF, Gainesville FL
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COLLABORATIVE DEVELOPMENT OF SOLAR ENERGY RELATED SOIL TREATMENT TECHNOLOGY

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ABSTRACT

For over 50 years, Army personnel have been engaged in a variety of operations involving the handling and disposal of toxic and hazardous materials. These operations have resulted in soil contamination at many active Army installations, as well as Army held properties which have been or are candidates to be declared excess land. Soil remediation must be performed before these contaminated sites can be reused or disposed of as excess land.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is responsible for the planning, implementation, and direction of the Department of Army Environmental Program under the Assistant Chief of Engineers. In support of this program, USATHAMA is conducting research to develop technology utilizing concentrated solar energy for the detoxification of soil contaminated with organic compounds. This project is a joint effort with the U.S. Department of Energy and U.S. Environmental Protection Agency.

Solar energy can be concentrated and used to destroy organic materials by thermal and photolytic degradation. Laboratory studies have shown destruction and removal efficiencies for solar powered detoxification systems can meet or exceed existing requirements for waste incinerators. This paper presents an overview of the joint solar soil detoxification program. Additionally, the results of a feasibility study of several solar and conventional soil remediation systems will be discussed.

INTRODUCTION AND BACKGROUND

On March 14th, 1992, representatives of the U.S. Department of Defense (DOD), U.S. Department of Energy (DOE), and the U.S. Environmental Protection Agency (EPA) met in Golden, Colorado. The purpose of this meeting was to initiate a collaborative effort to develop soil remediation technology utilizing solar energy for the destruction of organic contaminants. Four types of contaminants - aromatic, chlorinated aromatic, chlorinated solvents, and petroleum products - were identified as the primary targets of concern for this project.

The three agencies have unique reasons for participating in this program. The DOD, through the U.S. Army, hopes to eventually use solar detoxification for soil remediation at a number of installations. The EPA has a fundamental interest in innovative remediation processes that may have potential for extensive application. DOE scientists have actively investigated solar detoxification since 1986. The DOE is also responsible for

the development of processes utilizing alternative energy sources. Ultimately, the DOD, DOE, and EPA will be at the forefront in transferring this revolutionary technology to end users.

The administration of this project is directed by a management committee composed of representatives from EPA's Risk Reduction Laboratory (RREL), DOE's Office of Conservation and Renewable Energy, and DOD's U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). The committee is a mechanism for the DOD, DOE, and EPA to provide guidance and to ensure that their interests in the program are maintained. Other organizations involved in the program are shown in figure 1.

DEMONSTRATING THE SOLAR DETOXIFICATION PROCESS

The ultimate goal of the tri-agency project is to design, build, and operate a full-scale demonstration system utilizing solar energy at a Army waste site by 1995. The work leading to the successful demonstration of the solar soil detoxification technology is being conducted in three phases. During the ongoing first phase, RREL and the DOE's National Renewable Energy Laboratory (NREL) are conducting sub-pilot scale testing using a high flux solar reactor in a laboratory environment. A mixture of organic compounds, typical of the waste stream likely to be desorbed at Army waste sites, is being used to determine the performance criteria for design of the pilot-scale system.

In the second phase, USATHAMA will build on the work by NREL and RREL by designing, constructing, and testing a pilot-scale system at an Army waste site. During pilot-scale testing, the solar detoxification process will be refined and the performance conditions identified for the third phase, full-scale demonstration testing.

The demonstration system (figure 2) will couple conventional soil desorption, contaminant storage and concentration, and emissions control processes to the solar destruction process. The use of contaminant storage will allow the desorption system to run while the destruction system does not have enough solar flux available to operate. By concentrating the contaminants, the flow rate from the storage system will be significantly lower than the flow from the desorption system. Therefore, the solar system can be downsized relative to the desorption system.

The demonstration system should ideally achieve destruction and removal efficiencies (DREs) of at least 99.9999% mandated by the Resources Conservation and Recovery Act (RCRA) for waste containing polychlorinated biphenyls, dioxins, and furans. The full-scale system should produce fewer productions of incomplete combustion (PICs) than conventional incineration, be capable of processing 100 to 1,000 pounds of soil per hour, and must be mobile or transportable. Performance and cost data from the demonstration test will be used to implement the solar technology where applicable.



PROJECT COORDINATION ORGANIZATIONS SOLAR DETOXIFICATION OF SOIL

Department of Defense

U.S. Army Toxic and Hazardous Materials Agency

Office of the Assistant Secretary of Defense for the Environment

Army Corps of Engineers Directorate of Research and Development

Department of Energy

Office of Conservation and Renewable Energy

National Renewable Energy Laboratory

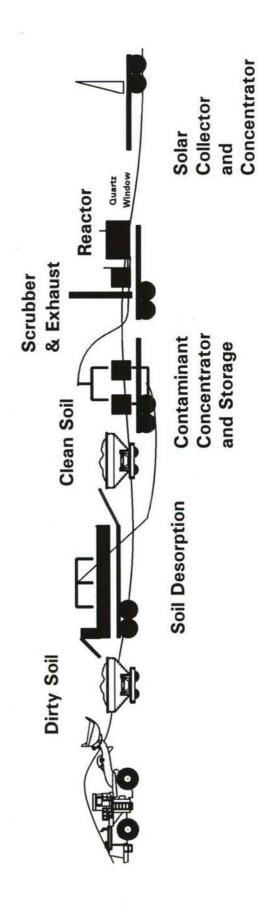
Environmental Protection Agency

Office of Research and Development

Risk Reduction Engineering Laboratory



Solar Detoxification of Soil Conceptual Drawing







THE FEASIBILITY STUDY

The specific study objective was to assess the potential feasibility of using solar energy for gas-phase destruction of toxic organic compounds desorbed from soil. Potential feasibility was considered based on a comparison of projected costs, performance, and applicability of several solar and conventual organic contaminant destruction processes.

Descriptions of the Solar Processes

The destruction of organic materials in the gas-phase can occur by catalytic, oxidative, photolytic, and thermal reactions. Typically, the compounds are converted to nontoxic by-products such as carbon dioxide, hydrogen chloride, and water. Photothermal oxidation (PHOTOX) uses concentrated sunlight to destroy contaminants by oxidative, photolytic, and, thermal reactions at approximately 1000 °C. Photocatalytic oxidation (PHOCAT) requires a catalysis to photolytically destroy contaminants at ambient temperatures. Solar assisted steam reforming (SOLTOX) makes use of concentrated sunlight to heat a rhodium metal catalyst to 700-100 °C. The contaminants undergo endothermic reactions on the rhodium with steam and are destroyed. Flow diagrams for these processes are shown in figures 3-5.

Solar Performance Effectiveness

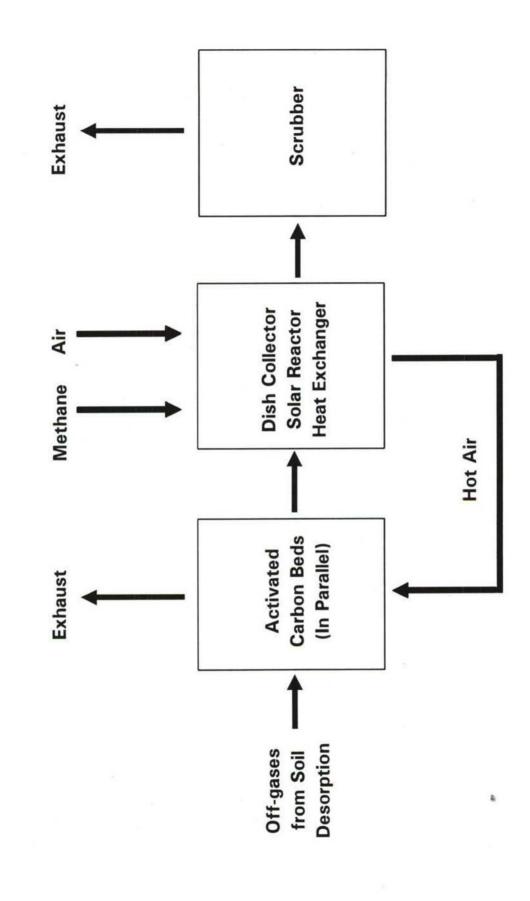
The goal of the performance assessment was to evaluate the potential for solar detoxification systems to offer performance advantages over conventional thermal oxidation for the destruction of organics in the gas-phase. Only the PHOTOX process was considered because it is more highly developed and tested than either PHOCAT or SOLTOX.

Laboratory and field studies have shown that the addition of concentrated solar radiation greatly improves the DREs for some organic compound relative to purely thermal conditions (Graham and Dellinger 1987; Dellinger et al. 1990; Glatzmaier et al. 1990a; Glatzmaier et al. 1990b; Graham et al. 1991). Based on the results of these tests, the PHOTOX process may be capable of achieving DREs of at least 99.9999% for many organic contaminants at temperatures significantly lower than the optimum operational temperatures for thermal oxidation systems. Laboratory studies have also indicated that solar processes may produce fewer PICs than thermal oxidation (Glatzmaier et al. 1990b; NREL 1991).

A major concern for solar detoxification processes is any disruption to the available solar flux. The disruption could be the result of a failure of the solar collection system or unanticipated cloud cover. For many compounds, a decrease in solar flux would result in reduced DREs because the solar processes are not designed to operation in the purely thermal mode. Therefore, solar remediation systems will require some type of back-up system to account for solar flux disturbances.

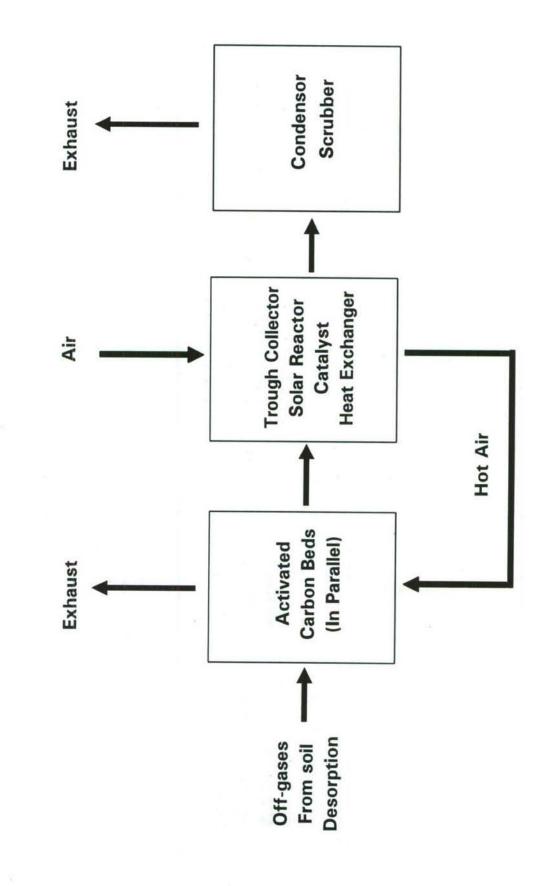
Another potential problem area for solar remediation systems,

PHOTOTHERMAL OXIDATION (PHOTOX)



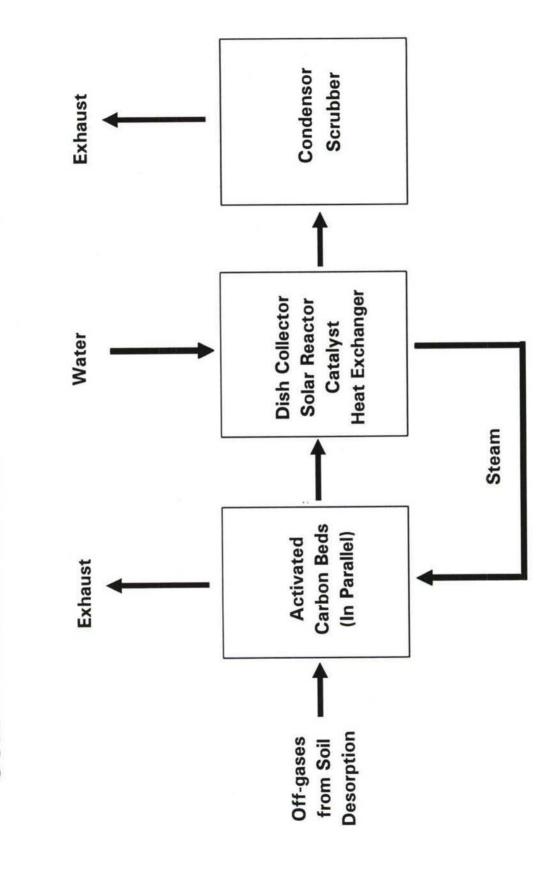


PHOTOCATALYTIC OXIDATION (PHOCAT)





SOLAR CATALYTIC STEAM REFORMING (SOLTOX)





is that many organic contaminants do not exhibit a photochemical effect. It is possible to add photochemical initiators to the wastes. However, the mixture of contaminants found at most remediation sites should be sufficient enough to initiate photochemical reactions with non-photoactive compounds.

Cost Effectiveness

Cost effectiveness was evaluated by conducting a review of a cost study completed by NREL (Glatzmaier 1991). The NREL study compared the solar processes to several conventional treatment methods (table 1) at several different trichloroethylene concentrations and flow rates. Trichloroethylene (TCE) was selected as the waste for this analysis because it is commonly found in contaminated soil.

The USATHAMA study considered each of the conventional processes except on-site recovery and thermal oxidation. Thermal oxidation was shown to be much more costly than thermal oxidation with activated carbon storage (THERMOX/AC). THERMOX/AC (figure 6) was cheaper than thermal oxidation because the volumetric flow rates from the carbon beds allowed the reaction vessel to be downsized. On-site recovery was not considered because it is not a destructive process. Catalytic oxidation (figure 7) could not be coupled to a concentration system because of the possibility of the catalyst being poisoned.

For the USATHAMA study, several assumptions were made:

- 1. The same desorption system would be used for the solar and conventional processes.
- 2. The TCE concentration and flow rate from the desorption system would remain constant.
- 3. The solar processes would be operational for 4 hours each day and the conventional systems would run continuously.

The estimated operational costs (dollars per pound of TCE) for each of the evaluated processes are shown in figure 8. The levelized costs - relative to PHOTOX - for the USATHAMA and NREL studies are shown in figure 9.

Findings of the Feasibility Study

THERMOX systems have been shown to be capable of achieving RCRA-mandated DREs for hazardous wastes (Hinshaw, 1989; EPA 1984). However, the solar processes may improve DREs and reduce PICs for some organic contaminants. The performance of the solar processes during unanticipated solar flux interruptions needs to be addressed.

The estimated production costs for the solar processes and THERMOX/AC were not significantly different. However, considerable uncertainty was involved in the design and costs associated with the treatment systems used for the cost analysis

Table

TREATMENT OPTIONS FOR ORGANIC CONTAMINANTS

SOLAR

Photothermal Oxidation

Photocatalytic Oxidation

Thermal Catalytic Steam Reforming

CONVENTIONAL

Off-site Carbon Regeneration

On-site Recovery

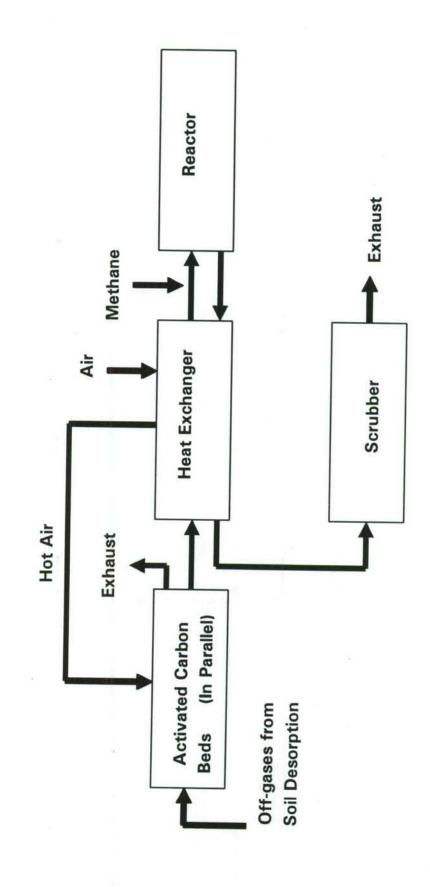
Thermal Oxidation with Contaminant Storage

Thermal Oxidation

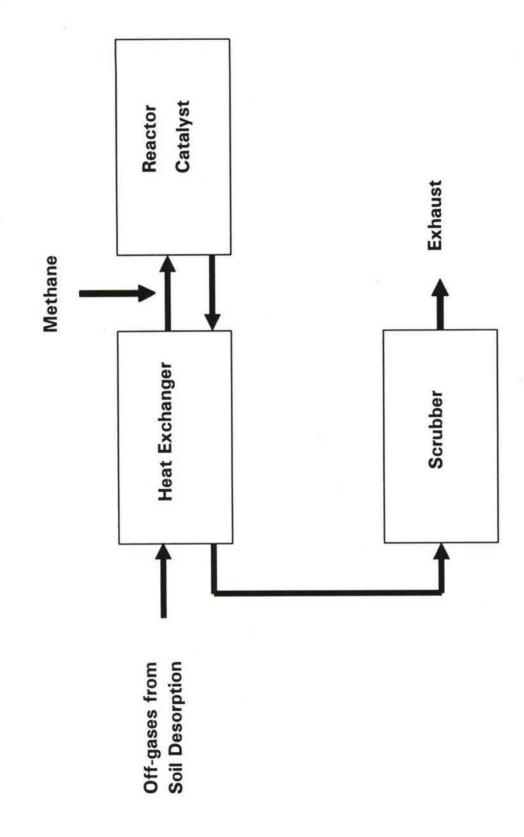
Thermal Catalytic Oxidation



THERMAL OXIDATION WITH ACTIVATED CARBON BEDS (THERMOX/AC)

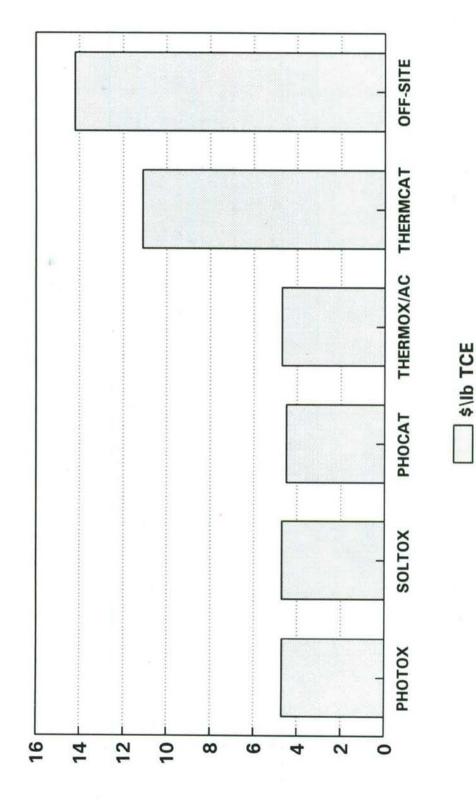


THERMAL CATALYTIC OXIDATION (THERMCAT)





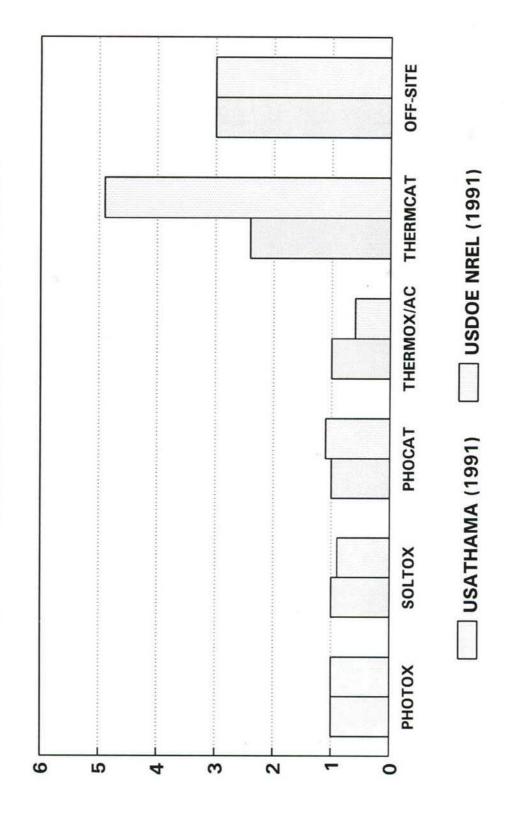
FOR TRICHLOROETHYLENE (TCE)* **ESTIMATED PROCESSING COSTS**



*In 1991 dollars



NORMALIZED PROCESSING COSTS FOR TRICHLOROETHYLENE*



*Normalized to PHOTOX estimated cost



CONCLUSION

Solar detoxification has the potential to achieve equal or better performance characteristics than conventional remediation methods for soils contaminated with organics. By collaborating on the development of this technology, DOD, DOE, and EPA are taking the lead in making a revolutionary idea a reality.

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DEVELOPMENT OF SOIL DECONTAMINATION TECHNOLOGY UTILIZING SOLAR ENERGY

FIELD DEMONSTRATION SITE SELECTION

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To successfully develop a new technology it is essential to conduct a field demonstration to test the system's effectiveness in a "true case" scenario. When using a field demonstration for a new technology system, it is most beneficial to have ideal site conditions, so that the system's highest level of performance can be determined. Although it is unrealistic to have ideal conditions, it is possible to select a site that can best accommodate such a system. Therefore, it was necessary to develop some means for selecting the best site to demonstrate the solar detoxification system.

Several criteria were used in the solar detoxification site selection process. The goal of the selection process was to target a hazardous waste site on an Army Installation that most closely met the pre-determined criteria. The first criteria, although seemingly obvious, was that the installation had to have some type of existing contamination. Identification of Army Installations that met this first criteria were identified by using the Installation Restoration Division Management Information System (IRDMIS). At this point, seventy Army Installations were identified to have existing contamination.

Next, a list was derived consisting of the top twenty-five organic compounds in soil determined to be most effectively detoxified by the solar system. The IRDMIS was used to identify Army Installations having contaminants from this list. The IRDMIS identified thirty-six Army Installations having at least one of the contaminants from the top twenty-five organic compounds solar detoxification list (Figure 1).

Because solar energy is the catalyst for this detoxification system, the best results can be observed when the sun's rays are most readily accessible. Therefore, to further narrow down the installation choices, a sunlight region in the U.S. was researched and selected. The outcome of this research discovered that there were nine Army Installations in the high sunlight region having at least one of the top twenty-five organic "solar detoxification" compounds (Figure 2).

The next step was to further classify the contamination that existed at the installations. A list was developed to determine what installations matching the above criteria, had sites that contained the top 8 solar contaminants. Again using the IRDMIS, the list of installations was reduced to five installations (Figure



FIGURE 1

TOP TWENTY-FIVE ARMY ORGANIC CONTAMINANTS FOR SOLAR DETOXIFICATION OF SOIL*

COMPOUND	NO. OF INSTALLATIONS
Toluene	36
Acetone	32
Methylene chloride	28
Trichloroethylene	27
Benzene	25
Ethylbenzene	24
Trichlorofluromethane	24
Tetrachloroethylene	23
Xylenes	22
Chlorobenzene	19
1,1,2-Trichloro-1,2,2-tri- fluroethane	17

*As identified in IRDMIS (9-16-91)

COMPOUND	NO. OF INSTALLATIONS
Phenol	14
1,1,1-Trichloroethane	12
1,2-Dichloroethenes	12
Methylethyl ketone	9
1,1-Dichloroethane	8
Carbon Tetrachloride	6
Methylisobutyl ketone	6
1,1,2-Trichloroethane	6
1,2-Dichloroethane	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	4
Vinyl Chloride	4



SOLAR DETOXIFICATION OF SOIL PROSPECTIVE TEST INSTALLATIONS

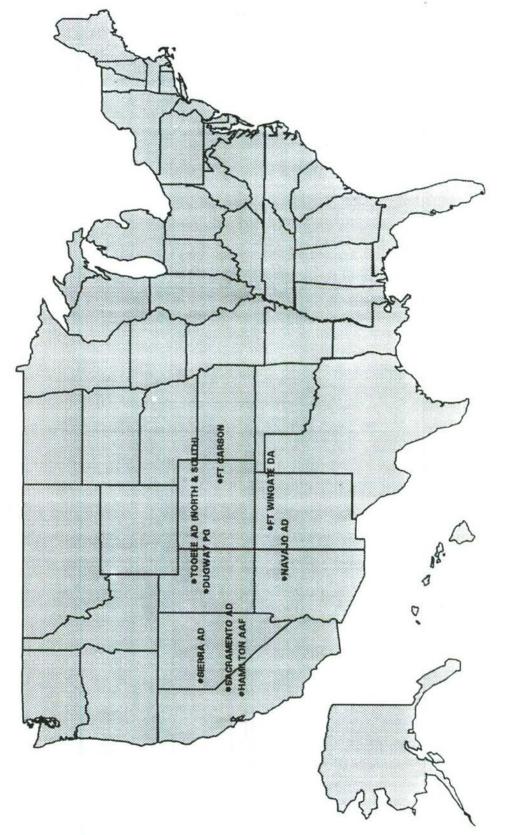
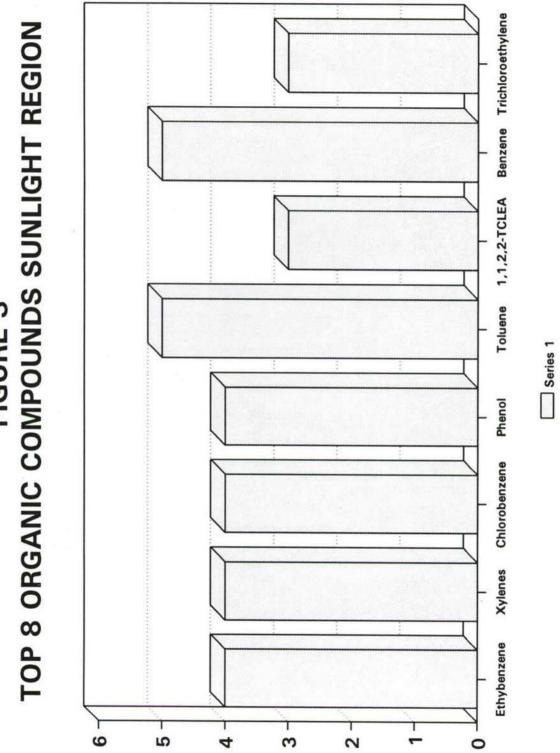


FIGURE 3 TOP 8 ORGANIC COMPOUNDS SUNLIGHT REGION





- 3). Finally, the actual hazardous waste sites on these five Army Installations were researched individually. Approximately 150 sites were reviewed. The following criteria was used to select the final site:
- (1) Contaminant Characteristics. Sites that have several of the top twenty-five organic "solar detoxification" compounds are considered more favorable. Furthermore, it is an important factor that the site have high levels of contamination, so results could be more easily measured. The solar detoxification system is not equip to destroy chemical agent or metals at this time. Therefore, these contaminants cannot be present at the site. However, at some time it is speculated that this system will develop technology to destroy petroleum, oils, and lubricants (POLs), and explosives. It may benefit the demonstration project to have access to a site on the selected installation that contains these contaminants.

(2) General Installation Characteristics. The installation must be easily accessible for equipment and personnel, etc.

(3) **Site Size.** To measure the effectiveness of the system, a minimum amount of contaminated soil is necessary. Therefore, the site had to have at least 25 cubic yards of contaminated soil.

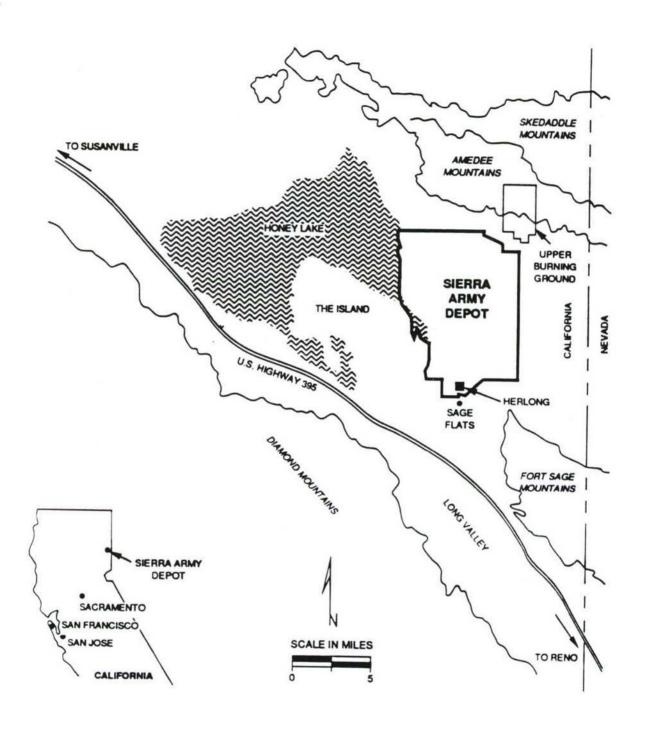
(4) Supporting Infrastructure. It was essential the selected site have easy access to electricity, buildings for storage of equipment, and other personnel supporting facilities.

- (5) Installation Support For Project. It is mandatory that the installation support the project. Use of buildings, land, and any special security clearances will need to be authorized by the installation. Furthermore, it is likely that the project will be visited frequently by interested parties. These visits will also need to be authorized by the installation.
- (6) Regulatory Requirements. Because the solar detoxification of soil system is an unproven technology, it cannot be used at sites where regulatory deadlines have been posed on the site and/or installation. No guarantees of performance can be given to the regulators, therefore it is necessary to find a site where there is time in the schedule to test the system.

After careful review of all the Army Installations and sites that were identified throughout the selection process, the site selected was the Defense Reutilization and Marketing Office (DRMO) Trench Area at Sierra Army Depot, Herlong California (Figure 4).

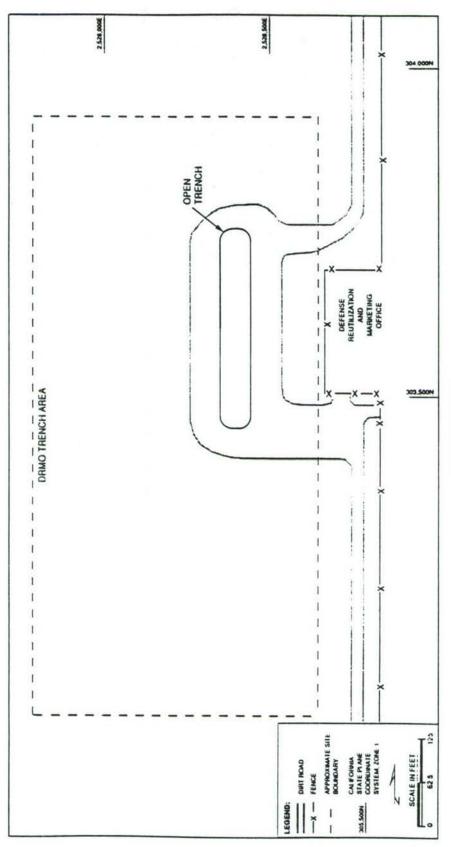
The DRMO Trench Area was used for the disposal of wood pallets, cardboard tubing, waste oil, sludge, and solvents (Benioff, et al., 1988: JMM 1991). The DRMO Trench was used extensively from 1942 to 1973 and in a limited capacity from 1973 to 1987 (JMM 1991). Between 1942 and 1973, approximately 90 liters per day of waste oils, oil sludges, solvents, and cleaning fluids were disposed of and burned in the DRMO Trench (USATHAMA, 1979: JMM 1991). The DRMO Trench Area consists of one open trench approximately 290 feet long by 40 feet wide and 10 feet deep (Figure 5) (JMM 1991).

Ongoing environmental investigations have shown contaminants at the site to include 8 volatile organic compounds (VOCs), 2 semivolatile organic compounds (SVOCs), and 5 pesticides. Seven of these contaminants have been detected above 100 parts per million (ppm) in the soil while 2 have been detected above 2,000 ppm. In



SIERRA ARMY DEPOT





SITE MAP: DRMO TRENCH AREA

FIGURE 5

addition, Trichloroethene and methylene chloride have been detected in the groundwater.

Investigations have also shown that most of the significant contamination lies within the south half of the trench. The depth of this contamination extends to about 30 feet below ground surface (20 ft below the trench opening). Although contamination has been detected in other locations of the DRMO Trench Area, the contaminated soil at southern portion within the trench will be of the most benefit for demonstration of the solar detoxification system.

Based on the comparisons and criteria developed for the site selection process, the DRMO Trench Area is most conducive to providing a successful atmosphere for the demonstration of the solar detoxification of soil system. After the demonstration is completed, USATHAMA will have a strong working knowledge of the system's capabilities and a method of how it will be used at other sites.

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TNT RED WATER TREATMENT USING WET AIR OXIDATION

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ABSTRACT

As environmental regulations become more stringent, minimization of ammunition wastewater (e.g., TNT red water) and/or its effective treatment and disposal have significant impacts on the operations of DoD ammunition facilities. Preliminary results showed wet air oxidation (WAO) to be effective for red water treatment. Additional experiments conducted at five different temperatures and three different initial oxygen pressures confirmed the earlier results: contaminant removal efficiencies are a function primarily of temperature and, to a lesser degree, of the initial oxygen pressure. For example, for 1:100 diluted red water the total organic carbon (TOC) and chemical oxygen demand (COD) removals at 260 °C (500 °F) and 90 psi (0.62 MPa) Poz were 77 and 91%, respectively, after 1-hr treatment; the corresponding removals were 94 and 99% at 320 °C and 90 psi Poz. The rate studies conducted under various experimental conditions showed a rapid initial reduction (within the first five minutes) in COD and TOC, presumably due to the oxidation of easily oxidizable compounds present in the red water.

Diluted raw red water (1:100) at a 20% fraction by volume in activated sludge showed significant toxicity to unacclimated heterotrophic bacteria, whereas the WAO-treated water (320 °C) at up to 75% fraction exhibited no effect. The treated red water, however, was found to be toxic to an unacclimated *Nitrosomonas* culture, indicating the possible formation of some toxic intermediates.

INTRODUCTION

The U.S. military has a complex industrial base with significant environmental impacts. Industrial wastewaters, such as those generated at the ammunition production and handling facilities, e.g., TNT red water, may often contain a variety of hazardous organic substances. In addition to the various soluble DNT sulfonated compounds, TNT red water contains products of incomplete nitration (e.g., priority pollutants 2,4-DNT and 2,6-DNT) and many complex byproducts formed during the nitration and purification stages. Currently, red water is regulated by the EPA (Environmental Protection Agency) as a Resource Conservation Recovery Act (RCRA) hazardous waste (KO47) due to its reactivity. Partially due to the environmental regulations, the US Army has not been able to produce TNT at its ammunition plants since circa 1986. The challenge of finding an environmentally safe and economically feasible alternative for treatment and disposal of the red water is of utmost importance.

A variety of processes are currently available for hazardous waste treatment (Cheremisinoff, 1988; PEI, 1990). The choice of which process is best suited to a waste stream depends upon the nature and concentration of the stream. The US EPA and the US Army have recognized wet air oxidation (WAO) as one of the most promising hazardous waste treatment technologies (EPA, 1984; PEI, 1990). Figure 1 is a conceptual relationship between process cost and concentration of organic pollutants (Roberts, 1973). A complete conversion (e.g., oxidation) to innocuous end products may be

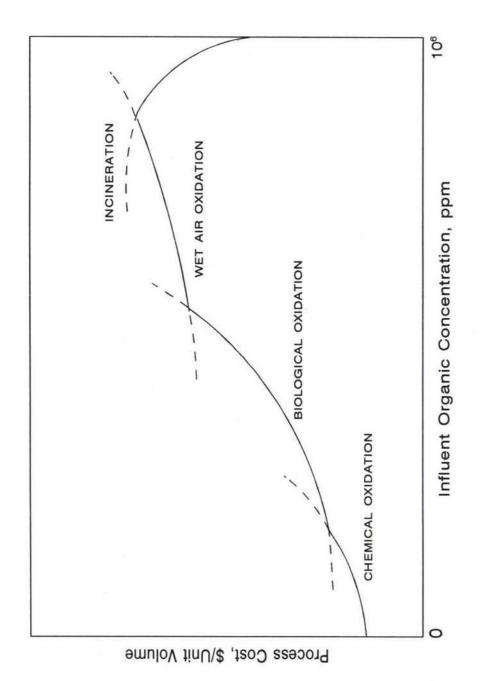


Figure 1: Process Cost as a Function of Organic Concentration (Roberts, 1973)

Table 1: Experimental Conditions Used for WAO Experiments

1-HR BATCH EXPERIMENTS:

Red Water Dilution = 1:100

P _{o2} , psi		T	emp., °C		
19	200	230	260	290	320
90	200	230	260	290	320
190	200	230	260	290	320

KINETIC EXPERIMENTS:

Dilution	Temp., °C	Poz, psi
1:100	260	190
	300	190
1:50	260	250
1:25	260	50
	260	100
	260	190
	260	200
	260	250
	260	350
	230	100
	280	100
	300	100
	260	250
	260	250

 $[\]dot{}$ with external addition of NaNO3 and Na2SO4

effectively achieved by conventional incineration for wastes containing more than 30% organics. However, the cost of incineration and the concomitant air pollution concerns sometimes limits its practical applications. Like incineration, carbon adsorption not only is energy intensive, but also creates a polluted waste stream (spent carbon) that needs to be regenerated or disposed. Biological treatment, which is by far the method of choice for a cost-effective treatment of concentrated biodegradable wastes, cannot successfully treat certain organic compounds due to their toxic, inhibitory, or refractory nature. Also, biological oxidation is quite sensitive to changes in waste concentrations (shock loads). The use of chemical oxidation for the ultimate degradation of organics, i.e., complete destruction to CO₂ and H₂O, may be suitable for organics at low concentrations, but may be extremely expensive for concentrated wastes. WAO, i.e., oxidation in the *aqueous* phase under high temperature (150 - 350 °C) and pressure (700 - 2500 psi), is ideally suited to liquid wastes which are too dilute to incinerate and too refractory to handle by chemical and biological oxidation, e.g., TNT red water.

The results of preliminary experiments showed WAO to be effective for red water treatment (Hao and Phull, 1991). For example, WAO of red water at 340 °C and 2150 psi resulted in almost complete oxidation of the oxidizable organic matter present; > 99% removals were achieved for both total organic carbon (TOC) and chemical oxygen demand (COD). The treated effluent had no detectable dinitrotoluene (DNT) sulfonates (2,4-DNT-5-SO₃Na, 2,4-DNT-3-SO₃Na, and 2,6-DNT-3-SO₃Na) and had only a trace amount of 1,3-dinitrobenzene (DNB). The effluent inorganic sulfate concentration increased significantly due to the oxidation of the organic sulfur present in red water. Accumulation of acetic acid was observed up to a WAO temperature of about 300 °C, after which the acetic acid concentration decreased due to further oxidation to CO₂ and H₂O.

In order to further define the WAO operational parameters for a practical and cost-effective application, additional experiments were performed at different temperatures and pressures. Kinetic experiments were conducted at different conditions to elucidate the effects of temperature, pressure, red water concentration, and salt concentration on the WAO removal rate of TOC, COD, and specific contaminants, e.g., DNT sulfonates. Microbial tests were conducted to determine the toxic effects of raw and treated red water on activated sludge (AS) and *Nitrosomonas*. The toxicity results should be helpful in determining the feasibility of integrating WAO with biological treatment, or in determining the suitability of direct discharge of WAO-treated red water to the receiving waters.

MATERIALS AND METHODS

MATERIALS

The red water used in this study was obtained from Canadian Industries Ltd., McMasterville, Quebec, Canada. The AS used in the toxicity tests was taken from an aeration tank at a local wastewater treatment plant and concentrated in the laboratory. The enriched *Nitrosomonas* cells were collected from a laboratory submerged nitrification column (Chen, 1991). Both AS and enriched *Nitrosomonas* cultures were unacclimated to the types of organics present in red water (i.e., sulfonated-and nitro-aromatics).

EXPERIMENTS

Experiments were carried out in a 2-liter T-316 stainless steel reactor (Parr Instrument) rated for temperature and pressure of up to 350 °C and 3000 psi. Experimental conditions used for the batch and kinetic experiments are summarized in Table 1. The apparatus shown in Figure 2 was used for the kinetic experiments to determine the concentration profiles with time under different experimental conditions.

Batch (1-hr) Experiments. The reactor was filled with one liter of diluted red water (1:100), charged with a known amount of O_2 , and sealed. It took 30-50 minutes to reach the desired temperature between 200 and 320 °C. At the end of each experiment (1-hr reaction time), the reaction

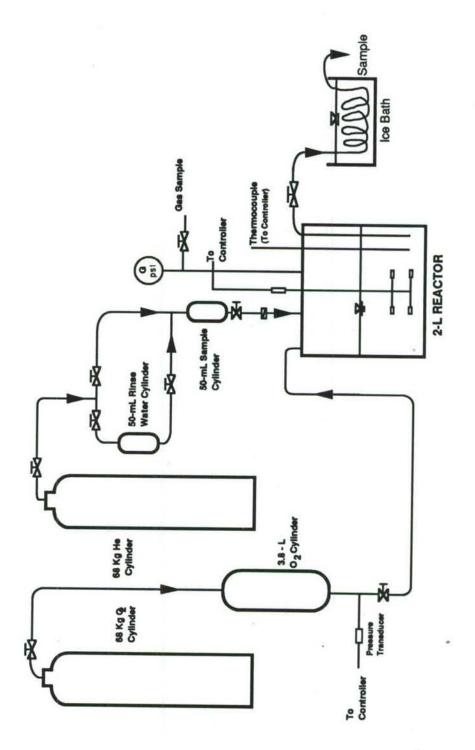


Figure 2: Schematic Diagram of Apparatus Used for WAO Experiments: Rate Studies

was quenched by cooling the reactor contents with tap water. It took 5-15 minutes to bring the temperature down to about 20 °C. The reactor offgas was slowly released under a laboratory hood. reactor was disassembled, and samples were withdrawn for analyses of the parameters shown in Table 2.

Kinetic Experiments. The reactor and the 50-mL sample and rinse water cylinders were filled, respectively, with appropriate amounts of distilled water, raw red water sample and distilled water. The respective amounts depended on the red water concentration to be studied. After sealing the reactor, a prescribed amount of O, was charged into the reactor and the contents were heated to a desired temperature. The impeller speed was maintained at 200-300 rpm. Once the desired temperature was reached, the raw red water sample was discharged (using He backpressure) into the reactor. The distilled water was then charged into the sample cylinder for rinsing and finally to the reactor for a total liquid volume of 1 L. The total run time was varied from 2 to 4 hours for different experiments. Samples were periodically withdrawn through a stainless steel coil that was submerged in an ice-water bath. The first sample was obtained within 5 minutes of sample injection. A small amount of liquid (10 mL) was discarded before each sampling event to minimize contamination from the liquid present in the dip tube and the sample collection loop. Samples were analyzed for COD, total volatile solids, pH, TOC and other parameters to assess the WAO efficiency.

Toxicity Tests. The concentrated AS sludge sample was split into five one-liter reactors. connected to individual air diffuser systems. The pH of treated red water was adjusted to 7 because of the initial low value (pH 3). A fraction of the sample and deionized water (supplemented with glucose and bicarbonate) were then added to the sludge for a final volume of 500 mL. Sludge samples were taken periodically and filtrate samples (Whatman GF/C filter) were used for COD analysis.

The enriched Nitrosomonas cells were concentrated in a centrifuge and redissolved in the feed medium (Chen, 1991). No attempts were made to acclimate the cells to nitroaromatics. The experimental procedures used were similar to those described above for heterotrophic COD degradation. The filtrate samples were analyzed for nitrite using the NDE dihydrochloride method (Standard Methods, 1985).

ANALYTICAL METHODS

A summary of analytical methods used is shown at Table 2; a complete description can be found elsewhere (Hao and Phull, 1991; 1992).

RESULTS AND DISCUSSION

BATCH EXPERIMENTS

COD, TOC, Total Volatile Solids (TVS), and Acetic Acid (HAc). A strong dependence of the reduction in TOC, COD, and TVS on temperature is apparent from the results summarized in Table 3. For example, COD reduction increased from 65% at 200 °C to 96% at 290 °C at Poz of 90 psi. Copa (1990) observed a 95% COD reduction at 300 °C in WAO experiments on red water in the 1950's. In the range of 90 - 190 psi, Poz appears to have insignificant effect on TOC/COD/TVS reduction; the effect becomes negligible even for Poz of 19 psi at higher temperatures. This indicates that Poz may not be a limiting factor and the small differences in the removal efficiencies may be due to the difference in the total system pressure, a finding previously reported by Chowdhury (1974) in uncatalyzed WAO of a brewery waste. The pressure effects were, however, not noticeable in catalyzed WAO under the same temperature and pressure conditions.

Acetic acid, one of the major known end products in WAO of organic compounds (Foussard et al., 1989) accumulated for temperatures up to 300 °C, after which its concentration decreased due to



TABLE 2: A SUMMARY OF ANALYTICAL METHODS USED

Parameter	Method	Instrument/Conditions Used
doo	Standard Methods (1985)	Acid/dichromate digestion, 2 hours reflux.
DNT sulfonates and NTSA	Reverse phase, ion- pairing Chromatography DL for NTSA = 0.1 mg/L	DIONEX IC model 2020i; MPIC-NSI analytical column with MPIC-NG1 guard and AMMS-1 suppressor; Eluant - 1mLmin 28% ACN + 2mM tetrabutylammoniumhydroxide (TBAOH); regenerant - 2-3 mL/min 0.025 N H ₂ SO ₄ ; column pressure - 1200 psi; sample size - 100 μL; Hewlett Packard model 3396A or Spectra Physics model 4270 integrator.
Inorganic Anions nitrite, nitrate sulfite and sulfate	lon Exchange Chromatography; DL = 0.1 mg/L for nitrite and 0.5 mg/L for others.	DIONEX IC model 2020i; HPIC-AS4A analytical column with HPIC-AG4A guard column and AMMS-1 suppressor; eluant - 2 mL/min 0.0028 M NaHCO ₃ + 0.0022 M Na ₂ CO ₃ ; regenerant - 2-3 mL/min 0.025 N H ₂ SO ₄ ; column pressure - 870 psi; sample size - 100 μL
acetate	DL = 0.1 mg/L	HPIC-AS1 analytical column with HPIC-AG1 guard column and AMMS-1 suppressor; Eluant - 2 mL/min 0.005 M Na ₂ B ₄ O ₇ ; regenerant - 2-3 mL/min 0.025 N H ₂ SO ₄ ; column pressure - 570 psi; sample size - 50 µL
Nitroaromatics α-TNT; 1,3,5-DNB; 2,4- and 2,6-DNT; NB; 1,3,5-TNB	Gas Chromatography. Aquepus samples (100 mL) extracted in 2 mL toluene by mixing at 30 rpm for 30 min. DL = 0.5 mg/L DL = 0.05 mg/L	Hewlett Packard GC model with model 3396A integrator; 10 m DB 1 column; electron capture detector (ECD); oven temp - 125 to 175 °C @ 5 °C/min; injector temp - 190 °C; detector temp - 200 °C; carrier gas (He) flow - 5-6 mL/min; make-up (Ar/CH ₄) flow - 30-35 mL/min; splittless injection; sample size - 1μL 8 m DB 1 column w/precolumn; oven temp - 75-140 °C @ 20 °C/min to 170 °C @ 4°C/min to 200 °C @ 5 °C; Injector temp - tracked 3 °C higher than oven temp; ECD temp - 250 °C; He flow - 5-6 ml /min Ar/CH flow - 30-35 ml /min co-column injection sample size - 1 μl
Н	Standard Methods (1985)	Orion pH meter model 501 with a combination pH electrode
Solids	Standard Methods (1985)	Total solids measured @ 103 °C, volatile solids measured @ 550 °C.
700	Acid/persulfate digestion. Infrared detection of CO ₂ produced. DL = 0.2 mg/L	O.I. TOC Analyzer model 700. (4.98 mL sample + 400 μ L 5% H_3PO_4 + 800 μ L 100 g/L sodium persulfate) digested for 5 min at 100 °C.

TABLE 3: WAO OF TNT RED WATER at P_{co} = 90 psi [@ 25 °C) AT DIFFERENT TEMPERATURES

Paw Operational Conditions Set Temp (S.T.), °C P _{ver} , psi P _{oz} at S.T., psi (Measured) P _T at S.T., psi (Measured) Total Solids (TS) TVS/TS, % NO ₂ TVS/TS, % NO ₂ NO ₃ So ₄ So ₅ So ₄ So ₆ So ₇ So ₇ So ₈ So	200 225 143 355 3.37 2420 867 1553 36 0 0	230 406 152 152 540 3.41 3.41 1607 30 693 693 693 0 0 275	3 280 680 161 161 805 3.27 3.27 1596 20 71	280 1079 170 1210 3.13 1833 247 1586 13	320 1638 179 1755 3.05 127 127 1646 7
(TVS)	200 225 143 355 3.37 2420 867 1553 36 0 0 230 0	230 406 152 540 3.41 2290 693 1607 0 0 275	260 680 161 161 805 3.27 1989 393 1596 20 71	290 1079 170 1210 3.13 1833 247 1586 13	320 1638 179 1755 3.05 127 127 1646 7
(TVS)	200 225 143 355 3.37 2420 867 1553 36 0 0 230 0	230 406 152 540 3.41 2290 693 1607 30 0 275	260 680 161 161 805 3.27 1989 393 1596 20 71	290 1079 170 1210 3.13 1833 247 1586 13 82	320 1638 179 1755 3.05 127 1646 7
(TVS) 3	225 143 355 3.37 2420 867 1553 36 0 0 230 0	406 152 540 3.41 2290 693 1607 30 48 0 275	680 161 805 3.27 1989 393 1596 20 71	1079 170 1210 3.13 1833 247 1586 13	1638 179 1755 3.05 127 1646 7
(TVS) 3	143 355 3.37 2420 867 1553 36 0 0 230 0	152 540 3.41 2290 693 1607 30 48 0 275	161 805 3.27 1989 393 1596 20 71	170 1210 3.13 1833 247 1586 13 82	179 1755 3.05 1773 127 1646 7 91
(TVS) 3	355 3.37 2420 867 1553 36 0 0 230 0	540 3.41 2290 693 1607 30 48 0 275	3.27 1989 393 1596 20 71	3.13 3.13 1833 247 1586 13 82	3.05 3.05 1773 127 1646 7 91
(JVS)	3.37 2420 867 1553 36 0 230 0	3.41 2290 693 1607 30 48 0 275	3.27 1989 393 1596 20 71	3.13 1833 247 1586 13 82 0	3.05 1773 127 1646 7 91
	2420 867 1553 36 36 0 230 0	2290 693 1607 30 48 0 275	1989 393 1596 20 71 0	1833 247 1586 13 82 0	1773 127 1646 7 91
(SVZ)	867 1553 36 36 0 0 230	693 1607 30 48 0 275	393 1596 20 71 0	1586 13 13 0	127 1646 7 91
	1553 36 36 0 230 0	1607 30 48 0 275	1596 20 71 0 271	1586 13 82 0	1646 7 91
	36 0 36	30 48 0 275	20 17 0 172	88 82 83	5 te 0
	30 0 36 0 230 0 0 36	48 0 275 0	0 271	8 0 85	. 6 0
	0 23 0	0 275 0	0 271	3 0 %	, 0
	230	0 275 0	271	0 000	0
	230	275	271	920	>
	0 0	0		220	336
	1001	>	0	0	0
	3	1068	1160	1208	1216
	31	49	09	09	8
	280	178	72	8	2
	65	78	91	96	66 ^
	255	228	112	22	8 8
MOVED	48	75	1	. 8	8 8
				3	5
	Q	0.11	90.0	0.10	0.13
	0.16	0.17	0.11	90.0	000
	0.25	0.35	0.0.7	0.05	0.00
2,6-DNT 0.02	0.49	0.72	0.36	Q	S
	12.31	3.74	0.91	0.83	0.32
1,3-DNB 0.04	7.02	21.50	21.33	17.55	7. S. R.
				2	3
	39	32	98	=	CN
2,4-DNT-5-SO ₃ Na	22	17	2	2	2 2

. ND (not detected)
. Estimated concentrations based on standards synthesized at our laboratory. A 100% yield was assumed and standards were used without further purification.



further oxidation to $\mathrm{CO_2}$ and $\mathrm{H_2O}$. Acetic acid is an excellent substrate for the microbes. Its presence in high concentrations at lower WAO temperatures suggests the possibility of integrating partial WAO with biological treatment, providing the partially treated red water is not otherwise toxic to the microbes. As discussed later, the high mineral concentration in treated red water is not expected to have adverse impact on the biological treatment of the WAO-treated red water.

Inorganic Sulfate and Nitrate. As expected, WAO of red water resulted in increased levels of sulfate due to the oxidation of the inorganic sulfite in addition to the oxidation of sulfonic (SO_3) groups associated with the organic DNT sulfonates and other SO_3 bearing organics such as the α -TNT-sellite complex. The increase in sulfur concentration (i.e., the difference between the sum of the sulfate and sulfite concentrations in raw and treated red water) was approximately 580 mg/L (as SO_4^2) at 200 °C and 820 to 890 mg/L (as SO_4^2) at 320 °C. As the exact composition of raw red water is not known, it is not possible to obtain an accurate sulfur balance. However, based on the significant increase in sulfate concentration and very low concentrations of volatile solids, COD, and TOC in the treated red water, it can be stated that in addition to DNT sulfonates, red water contains significant amount of other SO_3 -containing organics which are also destroyed under the WAO conditions studied.

Conversely, the nitrate concentration after treatment was in some cases less than the combined concentrations of nitrite and nitrate initially present in red water, thus raising questions about the fate of the nitroaromatics initially present in red water or those formed as WAO byproducts. Preliminary results indicate the presence of ammonium in the aqueous samples and N_2 in the reactor offgas. Similar findings for WAO of red water were recently reported by Copa (1992), who had earlier detected NO and N_2 during the WAO of propellant wastes (Copa and Randall, 1990).

Nitroaromatics. Although the data (Table 3) for nitrobenzene (NB) and 2,4,6-trinitrotoluene (α -TNT) are somewhat scattered, they generally show that the α -TNT concentration decreased with increasing temperature, whereas the NB concentration increased. The concentrations of 1,3-DNB, 2,6-DNT, 2,4-DNT and 1,3,5-trinitrobenzene (TNB) first increased and then decreased as the temperature increased from 200 to 320 °C, suggesting that these compounds may be intermediates formed during the WAO of red water. It is postulated that 1,3-DNB is formed during the WAO of red water from the oxidation of 1,3,5-TNB, from the oxidation of the DNT's which are produced from the desulfonation of DNT sulfonates, or both. The highest initial P_{o2} resulted in the lowest 1,3-DNB concentration. The general shapes of the curves for 1,3,5-TNB and 1,3-DNB (Figure 3) tend to support the above statement. The 1,3,5-TNB is initially present in red water and is also formed during the WAO of red water, from α -TNT and perhaps from the conversion of the so-called α -TNT-sellite complex.

It is noted that both NB and DNB are toxic substances; NB is listed as a priority pollutant. Attempts, therefore, must be made to eliminate the nitroaromatics from red water to the extent possible and practicable. Integration of partial WAO with biological treatment is certainly an alternative that should be further investigated.

DNT Sulfonates. The destruction of DNT sulfonates (Table 3) is also a function of temperature; the effect of pressure is not as clear. Removal efficiencies of 23% and 38% were achieved for 2,4-DNT-5-SO₃Na and 2,4-DNT-3-SO₃Na, respectively, at 230 °C and P_{O2} = 90 psi. The 2,4-DNT-5-SO₃Na was completely destroyed at 260 °C whereas complete destruction of 2,4-DNT-3-SO₃Na required a much higher temperature, i.e., > 290 °C. The relatively lower removals for 2,4-DNT-3-SO₃Na are probably due to the greater steric effects (Gilbert, 1978).

pH. A significant pH drop occurred in all WAO experiments, probably due to the formation of free mineral acids, the production of acetic and other low molecular weight organic acids, and the high concentration of aqueous CO_2 . The pH decrease is clearly a function of operating temperature and P_{02} . The final pH varied from 5.64 (320 °C and P_{02} = 19 psi) to 2.98 (320 °C and P_{02} = 190 psi).

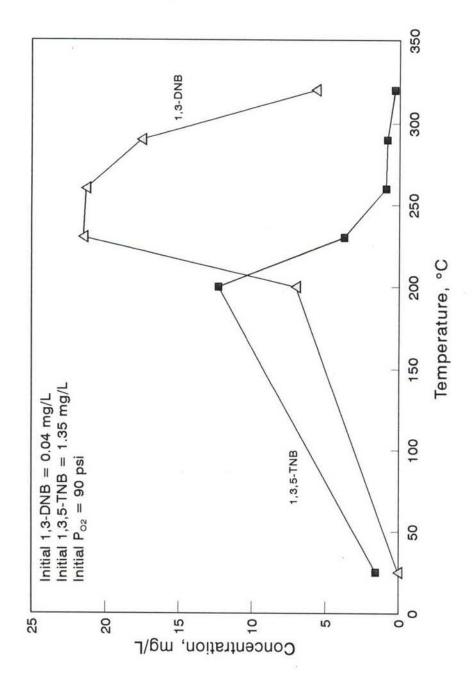


Figure 3: Concentrations of 1,3-DNB and 1,3,5-TNB as a Function of Temperature

KINETIC EXPERIMENTS

Typical profiles of COD, TOC, and TVS as a function of time are shown in Figure 4. A sharp reduction in the contaminant concentration during the initial period of reaction is due to the oxidation of easily oxidizable organics in red water. After the initial fast reaction, the reaction proceeds as a first-order reaction

$$r = - dC/dt = k[C]$$

where r = the rate of reaction, mg/L-min, C is the concentration (TOC, COD or TVS), mg/L, and k is the first-order rate constant, min⁻¹.

Effect of Temperature. As shown in Figure 5, the WAO temperature strongly influenced the rate of COD removal. In addition to the initial sharp COD reduction discussed above, there appear to be two more distinct phases at higher temperatures. This is perhaps due to the presence of a variety of organic compounds in red water which are oxidized at different rates under different experimental conditions. The Arrhenius plot for the rate constants in the first phase provided an activation energy of 16.3 kcal/mol (COD). This value is quite similar to the values cited for some specific organics, e.g., 16.1 kcal/mol for WAO of acetone (Taylor and Weygandt, 1974), 13.7 kcal/mol for catalytic WAO of phenol (Katzer et al., 1976), and 10.8 kcal/mol for WAO of phenol (Joglekar et al., 1991).

Effect of Oxygen Pressure. Experiments were conducted at five different initial P_{oz} (Table 1). The sharp initial reduction in COD and TOC, discussed above, was noticed at all oxygen pressures studied. The degree of initial COD or TOC reduction was proportional to P_{oz} . The subsequent reaction was first-order with respect to the substrate and was not influenced by the initial P_{oz} . Similar to the observations made at higher temperatures, two distinct first-order removal phases were present at the highest oxygen pressure (350 psi).

Effect of Red Water Concentration. Essentially the same phenomena were noticed for the experiments conducted at three different red water dilutions (1:100, 1:50, and 1:25): a rapid initial COD removal and a subsequent first-order reaction. The first-order rate constant was independent of the initial red water concentration.

Effect of Salt Concentration. Inorganic salts, e.g., Na₂SO₄, are not destroyed by WAO; their concentrations may actually increase significantly as described abovein the case of red water. In order to simulate the higher concentrations of salts under continuous treatment conditions, two experiments were conducted by adding 1.6% salt (15 g/L Na₂SO₄ and 0.6 g/L NaNO₃) to the red water sample in one experiment and 5.2% salt (50 g/L Na₂SO₄ and 2.0 g/L NaNO₃) in the second experiment. Slightly enhanced COD and TOC removal rates resulted in both cases, the enhancement being more noticeable at higher salt concentration. One possible explanation is that multivalent metals were present in the added salts as impurities in amounts large enough to catalyze the reactions.

TOXICITY TESTS

Diluted red water (1:100) at a 20% fraction by volume showed significant toxicity to unacclimated, heterotrophic bacteria in AS. However, batch COD removal capability in all four mixtures containing different fractions of treated red water was practically identical to that of the control, indicating that up to a 75% fraction of treated red water exhibited no inhibitory effects. This is not surprising since the treated red water at 320 °C and 90 psi contained very low concentrations of COD and TOC, and activated sludge has a large capacity to resist toxic effects from the trace amounts of residuals.

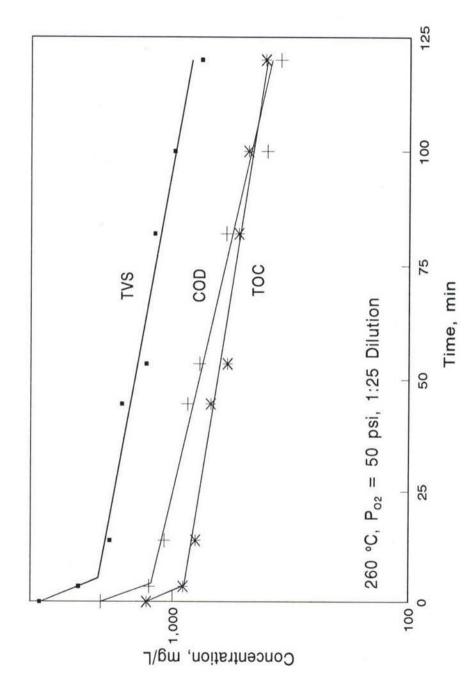


Figure 4: Typical TOC, COD, and TVS Removal Profiles for WAO of Red Water

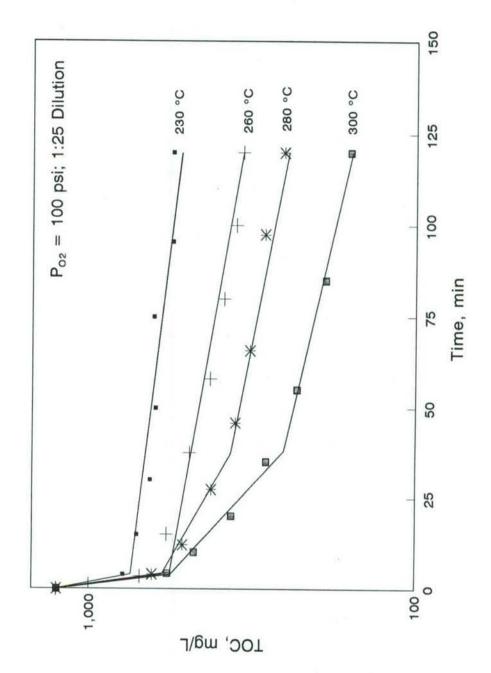


Figure 5: Effect of Temperature on WAO of Red Water: TOC Removal

The nitrite production with time from the *Nitrosomonas* culture is illustrated in Figure 6 for different fractions of treated red water added. For the control experiment, ammonium was completely oxidized to nitrite within a short period, with a zero-order rate of 0.28 mg N/L-min. Clearly, the nitrite production rates were significantly affected by the addition of treated red water: a 12% fraction of treated red water resulted in a 50% reduction of the nitrite production rate. The diluted raw red water (1:100) at up to 4% fraction, however, did not exert any noticeable effect on the nitrite production rate.

Based on the WAO removal efficiencies discussed earlier (i.e., > 90% removal for COD, TOC, and specific organics), a 4% fraction of the diluted raw red water would contain more of the organic compounds (COD = 22 mg/L) initially present in red water than the 12% fraction of the treated red water (< 1 mg/L COD). Consequently, it is reasonable to state that the observed adverse effects on *Nitrosomonas* culture are perhaps due to the byproducts formed during the WAO of red water. The major byproducts are, of course, inorganic sulfate and nitrate, although some organics and unknown chemical transformation products are also present. Additional toxicity tests with higher salt concentrations (400 mg/L NaNO₃ and 1500 mg/L Na₂SO₄ added to 1% fraction of diluted (1:100) red water) showed no adverse effects on the *Nitrosomonas* culture. The organic products (e.g., NB) formed during WAO of red water must, therefore, be responsible for the observed effects. For *Nitrosomonas*, the 50% inhibition concentrations (IC_{so}) of NB and 2,6-DNT have been estimated at 0.9 mg/L and 180 mg/L, respectively (Blum and Speece, 1991). It is noted that Keen and Baillod (1985) also reported the end products of the WAO of phenol, 2-chlorophenol, and 4-nitrophenol to be more toxic than expected, based on known residual concentrations of starting compounds.

CONCLUSIONS

The results of WAO experiments with the diluted red water (1:100) at five different temperatures and three pressures indicate that contaminant removal efficiencies are a function of temperature, and to a lesser extent, oxygen pressure. At the upper temperature limit of 320 °C and P_{02} = 190 psi, only small amounts of COD (8 mg/L), TOC (30 mg/L), HAc (38 mg/L), and TVS (127 mg/L) remained after a 1-hr reaction time. Additionally, some byproducts such as 1,3-DNB (5.7 mg/L) and nitrobenzene (0.13 mg/L) also existed. Significant accumulation of inorganic sulfates as well as the low TOC of treated red water indicate a high degree of desulfonation of DNT sulfonates and other sulfonated compounds; the SO_3 groups to SO_4^{2-} and organics to CO_2 .

Kinetic experiments revealed several interesting points. Under all experimental conditions, a sharp reduction was noticed in TOC, COD, and TVS in the initial reaction period due to the oxidation of easily oxidizable compounds present in the red water. The degree of "flash" COD or TOC reduction in the beginning was proportional to the WAO temperature and initial P_{oz} . After this fast oxidation, the reaction of the slowly oxidizable compounds proceeded at a typical first-order rate with respect to the substrate. Under more stringent WAO conditions, however, there were two distinct first-order rate phases. Temperature, as expected, significantly affected the first-order rate constants; the activation energy was approximately 16.3 kcal/mol (COD).

Up to 75% fraction (by volume) of treated red water (320 °C, 90 psi P_{o2} @ 25 °C) had no adverse effect on the capability of unacclimated heterotrophic activated sludge to remove glucose COD. However, the same treated red water sample definitely affected the nitrite production capability of the unacclimated enriched *Nitrosomonas* culture. Approximately 12% fraction of treated red water reduced the nitrite production rate by one half. Up to 1% and 4% fractions of the diluted raw red water (1:100), with and without the supplemental addition of NaNO₃ (400 mg/L) and Na₂SO₄ (1500 mg/L) did not exert any noticeable adverse effects on the *Nitrosomonas* culture. It is concluded that organic byproducts formed during the WAO of red water are responsible for the observed toxic effects. Consequently, a direct discharge of WAO-treated red water into the receiving waters may exert toxic effects on the aquatic life.



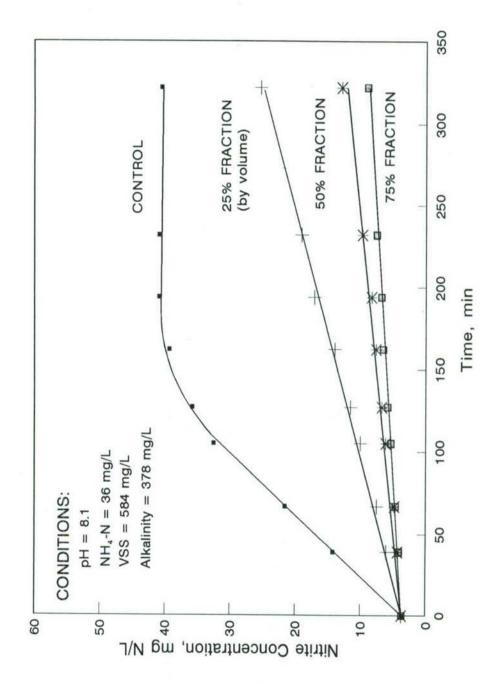


Figure 6: Toxicity of Trated Red Water (320 °C, 90 psi Poz) for Nitrosomonas

Additional research is needed to address the following factors to fully evaluate WAO as a practical and cost-effective technology for red water treatment: use of catalysts to enhance the reaction rates; further evaluation of the treated water toxicity to include adaptation of the microbial cultures to the constituents present in treated red water and to ensure safety of discharge into the receiving waters; integration of partial WAO treatment with other types of treatment such as biological; and complete characterization of reactor offgas to determine air pollution abatement requirements, if any.

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TREATMENT OF NITROGLYCERIN WASTEWATER WITH ACTIVATED CARBON

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Abstract

A military explosives manufacturing plant has developed a wastewater treatment system for removing nitrate esters including nitroglycerin (NG) and propylene glycol dinitrate (PGDN) from wastewater. Contamination is reduced from over 1000 to 1 mg/L. Granular activated carbon is employed in commercially available modular adsorbers containing 91 kg of carbon per unit. Four units are used in series to achieve the desired level of removal and to allow for leakage of contaminants ("breakthrough") from the leading adsorption modules as they approach saturation. Serial rotation of adsorption modules maximizes contaminant loading and minimizes carbon usage.

Activated carbon has previously been considered incompatible with NG due to NG degradation on the carbon, resulting in the formation of nitric oxide and other gases. As part of this project explosive safety was demonstrated, material management techniques were developed, gases were characterized, and disposal techniques were investigated. Regeneration of the carbon was found to be impractical, and incineration following aging of the spent carbon was chosen.

A full-scale system was designed and installed at five sites, treating up to 76 L/min continuously at each site. Design criteria were developed for pumping NG-contaminated wastewater with unspecialized inexpensive equipment.

Background

Explosive nitrate esters are both produced and used as propellant ingredients at the Indian Head Division, Naval Surface Warfare Center, Indian Head, MD. Wastewaters resulting from three processes contain various nitrate esters as well as a variety of organic and inorganic contaminants (Table I).

TABLE I. NITRATE ESTER WASTEWATER CHARACTERISTICS

Operation	Nitrate ester	Typical conc. range (ppm)	Other contaminants
Biazzi	Nitroglycerin (NG)	1-1800	Na ₂ CO ₃ , NaNO ₃ , Na ₂ SO ₄ , 2-nitrodiphenylamine, nitroaniline, ethyl centralite, resorcinol, triacetin, lead-2-ethylhexoate, di-n-butyl sebacate
	Propylene glycol dinitrate (PGDN)	1-3000	Na ₂ CO ₃ , NaNO ₃ , Na ₂ SO ₄ , dibutyl sebacate, 2-nitro- diphenylamine, resorcinol
Extrusion	NG	1-1200	FeO, lead and copper salicylate, lead and copper betaresor- cylates, 2-nitrodiphenylamine
Moser	Trimethylolethane trinitrate (TMETN)	1-600	Na ₂ CO ₃ , NaNO ₃ , Na ₂ SO ₄ , ethyl centralite, resorcinol, 2-nitrodiphenylamine
	Triethyleneglycol dinitrate (TEGDN)	1-6000	Na ₂ ,CO ₃ , NaNO ₃ , Na ₂ SO ₄ , ethyl centralite, resorcinol, 2-nitrodiphenylamine

In response to the State of Maryland's NPDES permit discharge limitations, Indian Head, in cooperation with the Maryland Department of the Environment, agreed to rapidly reduce our nitrate ester discharges to less than one part per million (ppm). To meet this requirement, the method of granular activated carbon (GAC) adsorption was chosen because it had been proven effective in treating waste streams containing propylene glycol dinitrate.

Because GAC had not been used for treatment of nitroglycerin or other nitrate ester waste streams, feasibility and safety studies were required. In addition, Indian Head had to determine the Department of Defense (DOD) and Department of Transportation (DOT) hazard classifications of the contaminated, or "spent," carbon resulting from the treatment process and develop the design parameters for a full-scale treatment system.

GAC Selection

Three steam-activated, low-ash GACs were selected and tested for adsorptive capacity (maximum loading), activation energy (low activation energy is evidence of increased instability), and the sensitivity of the spent carbon. The activation energy for thermal decomposition was determined by applying the maximum temperature of decomposition at different heating rates using Kissinger's equation:

$$(B/T^2) \times (E/R) = A \times \exp(-E/RT)$$

where:

B = heating rate (K/min)

T = peak temperature of the decomposition reaction

E = activation energy required for thermal decomposition

R = universal gas constant

A = frequency factor.

The results are shown in Table II. All the samples were insensitive to impact, friction, and electrostatic discharge (ESD). Based on these data, the Barneby and Sutcliffe type PC was chosen because of its lower adsorptive capacity and higher activation energy.

TABLE II. PROPERTIES OF CANDIDATE GACS

Candidate	Thermally	S	Spent carbon nitrate ester		
Caroloate	regenerable	NG	PGDN	TMETN	TEGDN
Barneby Sutcliffe PC	No				
Maximim loading ¹		44.6	76.2	51.1	55.0
Activation energy (kcal/mol)		27.0	34.1	45.1	32.2
Calgon F300	Yes			2535	
Maximum loading ¹	083987	54.0	86.1	81.4	23.4
Activation energy (kcal/mol)		27.7	33.4	41.4	35.2
Norit Aquarium	_	100000			00.2
Maximum loading ¹		28.3	43.8	20.2	20.5
Activation energy (kcal/mol)		16.8	41.2	30.6	14.1

¹ From laboratory-scale tests; given in nitrate ester per dry weight of carbon.

Hazard Classification (Sensitivity Testing)

Spent carbon was generated by passing wastewater through type PC carbon using 10- and 25-cm vertical columns constructed from PVC drain pipe. The typical feed rate was 130 L/min per square meter of cross-sectional area. The generated spent carbon was drained, dried to various degrees, and subjected to sensitivity testing. The tests showed that the carbon was completely inert when the moisture content exceeded 15% by weight (Table III). Drier carbon exhibited some nonpositive smoking and burning during the impact, ESD, and friction tests, but the samples were not fully consumed and the reactions did not go to completion.

TABLE III. RESULTS OF MOISTURE VERSUS SENSITIVITY TESTING

Nitrate ester	Lowest moistu	re content where no re	eaction was detected (% water
INITIALE ESTEI	Impact	Sliding friction	Electrostatic discharge
NG	15	13	10
PGDN	11	3	13
TEGDN	3	9	3
TMETN	11	13	3

Spent carbon at 15% water content was then subjected to the DOT thermal stability test and DOD explosive tests. The thermal stability test called for in 49 CFR 173.21 is based on ANSI Standard Method E 487-79. The test was performed at 54.5 °C using 100-g samples. Virgin carbon was used as a thermal blank for comparison. A temperature difference greater than 1 °C above the blank constituted a failure. Spent carbon samples generated in the nitration plant containing NG, PGDN, and TEGDN passed the test. NG carbon from the extrusion plant failed with a 5 °C exotherm. Extrusion carbon required 1 month of aging to pass. The carbon samples passed the DOD explosive tests of cap, card gap, and unconfined burn. Based on these results, the spent carbon was classified as a nonexplosive. The interim DOT classification is Class 9; Environmentally Hazardous Substance, solid, N.O.S.; UN No. 3077.

Pilot-Scale Testing

Our full-scale system was to consist of a series of commercial columns each with a bed depth of 0.8 m. Our criterion was 75% exhaustion of the first column with 1 ppm maximum nitrate esters after the last column in the train. To provide data for the full-scale system, a pilot-scale system was built with 2.5-cm-diameter columns with 1.5-m bed depths. The columns had sample ports at 0, 0.19, 0.38, 0.57, 0.76, and 1.52 m of carbon bed. The concentration at various bed depth versus time data collected from operating these columns were used to determine the minimum carbon bed depth required for the full-scale system.

The results are summarized in Table IV. The NG wastewater data indicated that 2.5 m of carbon bed depth was needed to assure 75% exhaustion of the first 0.76 m of carbon without breakthrough of greater than 1 ppm. This criterion required four canisters to handle a 37.8-L/min stream.

TABLE IV. TOTAL GAC BED DEPTH REQUIRED

Nitrate ester	Service time (hr)	Total bed depth (m)
NG (1,000 ppm)	17.8	2.5
PGDN (1,000 ppm)	23.3	1.3
TEGDN (3,941 ppm)	7.8	1.8
TMETN (255 ppm)	66.5	1.5

Full-Scale System

Based upon a hazard analysis of the proposed wastewater system and Indian Head's 25 years of experience with nitrate ester manufacture, a series of design parameters for safe operation was developed. The canisters chosen are commercially available carbon adsorbers containing 90.7 kg of GAC. They are fabricated from 55-gal DOT 5B drums.

The wastewater collection system (Figure 1) is a settling tank with a long enough retention time to assure that any free nitrate ester settles out and is not passed through the carbon columns. A surge tank acts as a feed reservoir for pumping the wastewater through the columns. Both the settling and surge tanks are designed to be free draining for collecting any coalesced nitrate ester and have no threaded bottom fittings.

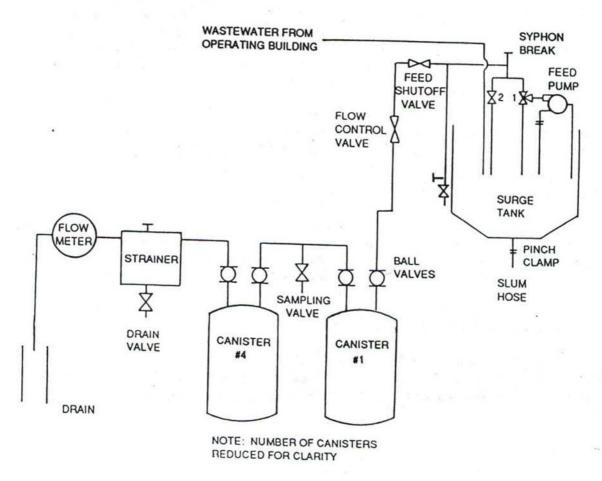




FIGURE 1. CARBON ADSORPTION SYSTEM

All wastewater analysis is performed using high performance liquid chromatography. The GAC treatment systems are monitored using a manual sampling protocol. At the end of each run a sample is taken between the third and fourth canisters. Drums are removed from the column train when this analysis reports 5 ppm. At this time the first column is removed, the remaining columns are moved up, and a new column is placed in the fourth position.

Eight sites were chosen for installation of the treatment system. Five sites have been in operation since August 1991. Indian Head is in compliance with the 1-ppm discharge limit.

AIDS TO EFFICIENT MANAGEMENT AND CONTROL OF ASBESTOS HAZARDS: SADS (SURVEY AND ASSESSMENT DATA SHEETS) AND THE COMPUTER DATA BASE MANAGER, ASAPS (ASBESTOS SURVEY AND ASSESSMENT PRIORITIZATION SYSTEM)

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ABSTRACT

The Asbestos Containing Material Survey and Assessment Data Sheets (ACM-SADS) is a comprehensive, algorithm-based form/checklist, which can be used to document in detail a survey and assessment of asbestos hazards at Army installations. It was developed by USA-CERL to meet the need for an easily understood, generally applicable form to be used Army-wide by either an in-house Army or outside contractor evaluator. The ACM-SADS incorporates terms used in the language of the Asbestos Hazard Emergency Response Act (AHERA), National Emission Standards for Hazardous Air Pollutants (NESHAP), 40 CFR Part 61, and terminology used throughout the asbestos management and control industry. The algorithm for the SADS is based upon the best features of several survey and assessment algorithms created and used by other government agencies and commercial firms.

While conducting a survey, an evaluator will complete the survey pages of the SADS, by recording the location (WHERE), the identity (WHAT) and quantity (HOW MUCH) of asbestos containing Surface Materials (SM), Thermal System Insulation (TSI) and Miscellaneous Materials (MM) found in a specific functional space. The evaluator will then perform an assessment (DAMAGE AND EXPOSURE POTENTIAL) by completing a set of assessment pages for each homogeneous ACM in the functional space. For most functional spaces, a completed SADS will consist of one set of survey pages and multiple sets of assessment pages.

The evaluator must be minimally an AHERA accredited inspector, if he or she is to complete the survey pages of the SADS. Completion of the assessment pages requires, in accordance with AR 200-1, the evaluator to be minimally an AHERA accredited Management Planner.

The SADS data can be used in conjunction with a matrix provided to determine an Assessment Index for any functional space. Management Planners can then hazard prioritize functional spaces and, in turn, facilities. Alternatively, Management Planners may use ASAPS, the data base management system developed by USA-CERL. ASAPS is user friendly and employs the PARADOX data base software, which requires only an IBM compatible PC. Once the information from the completed SADS is entered into the data base, it is stored and can be augmented, retrieved, edited, sorted and processed to generate reports in many formats. The Assessment Index is automatically determined.

INTRODUCTION

The U.S. Army ACM Survey-Assessment Data Sheet (USA ACM-SADS) presented and described in this paper has been developed by USA-CERL to meet the need for an easily understood, generally applicable form to be used Army-wide by either in-house Army personnel or outside contractors.

The USA ACM-SADS incorporates terms used in the language of the Asbestos Hazard Emergency Response Act (AHERA). AHERA, which has been recently revitalized by the Asbestos School Hazards Abatement Reauthorization Act (ASHARA), is applicable to the inspection of all public and private primary and secondary schools and is not applicable to other public and private buildings. Some AHERA terminology, however, such as "functional space," "thermal system insulation," and "management planner," has been incorporated in the SADS, because it is recognized, well-understood and used throughout the asbestos control and management industry. The remainder of the terms used in the SADS are also well-understood and commonly used.

A survey is defined in this paper as the inspection of functional spaces to locate, identify and measure the amount of ACM present. An assessment further evaluates the ACM in terms of (1) its potential to be airborne, or the actual extent to which it is a source of airborne fibers (damage), and (2) to what extent humans are exposed to airborne fibers in the functional spaces of a facility containing asbestos (exposure). Army asbestos management programs will include as assessment with any survey conducted.

The ACM-SADS is a form which consists of four different types of pages. Figure 1(a) is the first page type. In addition to serving as the title page, it is used to record general information and survey data. Because the first page contains Section A of the SADS, it is referred to herein as the "section A page." The second page type, Figure 1(b), is dedicated to the recording of survey data. It is referred to as the "section B page." The remaining two page types, Figures 1(c) and 1(d), are dedicated to recording assessment information; they are respectively referred to as the "section C page" and "section D page". A single SADS, containing one or more of each of the four page types, is used to evaluate (survey and assess) all the ACM in one functional space.

While conducting a survey, the evaluator will complete the survey pages of the SADS, section A and B pages, by recording the location (WHERE), the identity (WHAT) and the quantity (HOW MUCH) of asbestos containing Surface Materials (SM), Thermal System Insulation (TSI) and Miscellaneous Materials (MM) found in a specific functional space. The evaluator will then perform an assessment by completing a set of section C and D pages for each homogeneous ACM in the functional space, which was listed in the survey section B.

The evaluator must be minimally an AHERA accredited Inspector, meeting the requirements of the ASHARA modified model accreditation plans, if he or she is to complete the survey pages (sections A and B) of the SADS. Completion of the assessment pages (sections C and D), requires, in accordance with AR 200-1, the evaluator to be minimally an AHERA accredited Management Planner.

Prior to commencing a survey-assessment of any functional spaces in a facility, the evaluator should have participated in Asbestos Management Team meetings during which inspection strategies and plans were discussed and written. Also, the evaluator should have

FIGURE 1(a)

US ARMY ACM SURVEY/ASSESSMENT DATA SHEET (ACM-SADS)

INSTALLATION:	INSPECTOR:	
DATE OF INSPECTION:	AFFILIATION:	
LOCATION INFORMATION Facility No./Description:		
Facility Purpose:	Drawing No.:	
Functional Space:		
A Survey - Functional Space	Characteristics	
(1) Ceiling type:		Height (ft):
Shape: ☐ Flat ☐ Folded	i plate □ Dome □ Barrel	3/ 0/1/
Drop Ceiling: Yes, Heigh	t (ft.): 🗆 No	
Land to the second seco	(3) Wails:	
(5) Machinery/Equipment:		
(6) Sketches and remarks as appropri	ate to describe functional space. (Attach additional	I ab a see 16
(0) Sacreties and Tematas as appropria	ate to describe functional space. (Attach additional	sneets if necessary.)
_		
		(9)

Faci	lity No./Descrip	tion	Functional S	pace	
В	Survey - ACM	Type/Quantity			
	Type of ACM	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			1
72.7	ACM function/form	n			-
(9)	Friable (Y/N)				<u> </u>
	Length (ft-in)				
	Width (ft-in)				
<u>e a</u>	Height (ft-in)				
	Diameter (ft-in)				
	Thickness (in)				
	Pipe O.D.(in)				
	Pipe ACM O.D.(in	N			
	Lagging type				
	# Fittings/Valves				
	Area (ft²)				
	Sample Nos.				
(20)	oumpie i looi				
(21)	Asbestiform				
(22)	Asbestos %				
Com	ments:				
Code					
(7)		urface Materials (SM), Therm	nal System Insulation (TS	D. Miscellaneous Mate	erials (MM)
(8)		orm: [Functions] [SM] (A) A			
,	(D) Potable water	, (E) Other cold lines, (F) Oth	her hot lines/steam, [MM]	(G) Roofing, (H) Gast	ket seal,
		oring, (K) Other; [Forms] (1) stock-paper/millboard, (6) Pr			
		titious, (11) VAT, (12) Other		weied, (6) Allcell, (9)	maisie,
(17)		A) Cloth, (B) Sheet metal, (E) Board, (F) Other	
(21)	Asbestiforms: (A) Chrysotile, (B) Crocidolite,	(C) Amosite, (D) Tremol	lite, (E) Actinolite, (F)	Anthophyllite
	Diene over 54		D. 4 777		
	INSPECTED BY	U	DATE		
		AHERA Inspector Accreditate Source And Most Recent Date			



FIGURE 1(c)

INSTALLATION:	MANAGEMENT PLANNER:
DATE OF ASSESSMENT:	_ AFFILIATION:
Facility No./Description	
Functional Space:	ACM Function/Form:
C Friable ACM Assessment - Damage/Damag	e Potential
(23) Physical damage to ACM. Rips, tears, gouges and/	or evidence of ACM debris on floor/work surfaces.
☐ High ☐ Moderate ☐ Low ☐ Mi	inimal None Localized Distributed
(24) Water damage to ACM.	☐ No ☐ Localized ☐ Distributed
(25) Proximity (P) of ACM to repair/routine maintenance	
A. Friable surface material [SM]. P < 1 ft. or or	AND A TOTAL OF THE PARTY OF THE
☐ 1≤P<5ft. ☐ P≥5ft.	☐ P≥5 ft. and no repair/maint.
B. Friable thermal system insulation [TSI].	server or Fig
Repair/maint. will damage ACM	☐ No damage likely
(26) Type of friable ACM:	104
	MM
Other non-friable ACM with exposed friable are	
(27) Potential for occupant contact with friable SM or od (a) Proximity < 10 ft. High Med	Control Contro
(28) Asbestos (%) content of ACM.	Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ Low
□ 1 < % ≤ 30 □ 30 < % ≤ 50 □ % > 50	☐ All samples, no asbestos
2301/0300 270/30	a Au samples, to accous
Comments:	
	*

	rional Space: ACM Function/Form:
·mic	ctional Space: ACM Function/Form:
D	Friable ACM Assessment - Exposure Potential
(29)	Friability of ACM.
	Area of visible friable surface material or other damaged friable ACM.
(30)	□ < 10 ft² □ 10 ≤ ft² < 100 □ 100 ≤ ft² < 1000 □ ≥ 1000 ft²
	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).
	□ <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥ 50
(31)	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.
(31)	□ Rough □ Pitted □ Moderate □ Smooth
(32)	Ventilation: check all categories that apply.
(32)	☐ ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airflow
	likely.
	☐ ACM in interior of return duct or plenum which is part of recirculating system.
	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainment potential.
	☐ None of the above apply.
(33)	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:
	☐ Turbulent air ☐ Moderate air streams ☐ Quiet air
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.
	☐ High (e.g., mechanical room) ☐ Med (e.g., forklifts, runway) ☐ Low (e.g., classroom, office)
(35)	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.
	☐ Carpet or other difficult-to-clean material ☐ Seamed or rough, hard surface ☐ Smooth, hard surface
	☐ Special (e.g., wood or dirt), roughness: ☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ Smooth
(36)	Barriers: ACM coverings.
	A. Surface Material (SM) on ceiling/walls.
	☐ Suspended ceiling or accessible secondary wall ☐ Encapsulation ☐ Railing or wire mesh ☐ Non
	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:
	$\square \le 25\%$ $\square 25 < \% \le 50$ $\square 50 < \% \le 75$ $\square 75 < \% \le 100$
(37)	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.
	$\square \le 9$ or for corridors $\square 10 \le pop \le 200$ $\square 201 \le pop \le 500$ $\square 501 \le pop \le 1000$
	□ ≥ 1001 or for medical facilities, youth centers, child care or residential facilities regardless of population



FIGURE 1(c)

INSTALLATION:	
DATE OF ASSESSMENT:	AFFILIATION:
Facility No./Description	
Functional Space:	ACM Function/Form:
C Friable ACM Assessment - Damage/Damage	ge Potential
(23) Physical damage to ACM. Rips, tears, gouges and	or evidence of ACM debris on floor/work surfaces.
☐ High ☐ Moderate ☐ Low ☐ M	linimal O None O Localized O Distributed
(24) Water damage to ACM.	☐ No ☐ Localized ☐ Distributed
(25) Proximity (P) of ACM to repair/routine maintenance	
A. Friable surface material [SM]. P < 1 ft. or	The state of the s
□ 1≤P<5ft. □ P≥5ft.	□ P≥5 ft. and no repair/maint.
	☐ Contaminated ceiling panel removal necessary
Repair/maint. will damage ACM (26) Type of friable ACM:	☐ No damage likely
	1 MM
Other non-friable ACM with exposed friable are	
(27) Potential for occupant contact with friable SM or of	
(a) Proximity < 10 ft. High Med	
(28) Asbestos (%) content of ACM.	
□ 1 < % ≤ 30 □ 30 < % ≤ 50 □ % > 50	☐ All samples, no asbestos
Comments:	
comments.	
	e vy R
v =	



Faci	lity No./Description
Func	ctional Space: ACM Function/Form:
D	Friable ACM Assessment - Exposure Potential
(29)	Friability of ACM.
	Area of visible friable surface material or other damaged friable ACM.
	$\Box < 10 \text{ ft}^2$ $\Box 10 \le \text{ft}^2 < 100$ $\Box 100 \le \text{ft}^2 < 1000$ $\Box \ge 1000 \text{ ft}^2$
	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).
	□ <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥ 50
	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.
	☐ Rough ☐ Pitted ☐ Moderate ☐ Smooth
	Ventilation: check all categories that apply.
	□ ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airflow likely.
	ACM in interior of return duct or plenum which is part of recirculating system.
	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainment potential.
	☐ None of the above apply.
(33)	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:
	☐ Turbulent air ☐ Moderate air streams ☐ Quiet air
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.
	☐ High (e.g., mechanical room) ☐ Med (e.g., forklifts, runway) ☐ Low (e.g., classroom, office)
(35)	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.
	☐ Carpet or other difficult-to-clean material ☐ Seamed or rough, hard surface ☐ Smooth, hard surface
	☐ Special (e.g., wood or dirt), roughness: ☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ Smooth
(36)	Barriers: ACM coverings.
	A. Surface Material (SM) on ceiling/walls.
	☐ Suspended ceiling or accessible secondary wall ☐ Encapsulation ☐ Railing or wire mesh ☐ None
	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:
	$\square \le 25\%$ $\square 25 < \% \le 50$ $\square 50 < \% \le 75$ $\square 75 < \% \le 100$
(37)	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.
	$\square \le 9$ or for corridors $\square 10 \le pop \le 200$ $\square 201 \le pop \le 500$ $\square 501 \le pop \le 1000$
	□ ≥ 1001 or for medical facilities, youth centers, child care or residential facilities regardless of population



been provided and be familiar with any available facility site plans, as-built drawings, previous inspection reports, abatement records and any other records, reports, plans or accounts relevant to the ACM survey-assessment.

Once a SADS has been completed for every functional space within a facility, an AHERA accredited Management Planner will compile and process the information. This information will allow the Management Planner to document and/or confirm the existence of homogeneous areas of ACM and very importantly, prioritize the facility in terms of its asbestos hazards relative to other facilities at an installation or command.

The assessment scheme in sections C and D of the SADS is identical to the algorithm shown and discussed in the appendix, with a few exceptions. The weighted numerical values corresponding to assessment choices in the algorithm do not appear in the SADS and some of the line-items in sections C and D contain additional assessment choices. Management Planners who want to hazard prioritize functional spaces and, in turn, facilities, based upon a numerical score ranking, should use the values for the assessment choices given in the appendix and the procedures discussed therein. Alternatively, Management Planners may use a data base management system developed by USA-CERL, called ASAPS, which is the acronym for Asbestos Survey and Assessment Prioritization System.

ASAPS is user friendly and employs the PARADOX data base software, which requires only an IBM compatible PC. Once the information from the complete SADS is entered into the data base, it is stored and can be augmented, retrieved, edited, sorted and processed to generate reports in many formats. The assessment information from the SADS is automatically processed to generate an assessment index in accordance with procedures provided in the appendix. For additional information on ASAPS, the point of contact at USA-CERL is Mr. Bernie Donahue, 217-373-6733.

INSTRUCTIONS FOR COMPLETING THE USA ACM-SADS

Depending upon the number of different kinds (types, functions and forms) of ACM in the functional space, the SADS may consist of a minimum of four pages, one each of the section A,B,C and D pages, or many pages. If the functional space is, for example, a boiler room with many different kinds of ACM, the SADS may consist of one or more each of section A and B pages and several each of section C and D pages, grouped in C-D sets.

Each page of the SADS has in the lower right corner a page number indicator, viz., Page of _ . Because the evaluation of a specific functional space may require you to complete multiple SADS pages, the page numbering is to be done by you. A complete SADS may, for example, consist of one section A page, three section B pages, listing a total of eighteen different kinds of homogeneous ACM and fifteen each of section C and D pages. You would number those SADS pages, Page 1 of 34 through Page 34 of 34.

All readily identifiable and suspect ACM in the functional space should be surveyed and listed in section(s) B of the SADS. You should assess, using section C and D pages, only those ACM listed on the section B page(s) which are either friable or damaged, non-friable. In the page numbering example, given in the previous paragraph, there were eighteen different kinds of ACM listed on the SADS section B pages. Only fifteen of the different kinds of ACM listed were assessed because three of the listings were for undamaged, non-friable ACM.

Figure 2, which consists of twelve SADS pages, labeled Figure 2(a) through 2(l), has been provided as an example of how to complete the form. You will notice it has been filled in by hand, with some comments and calculations written in the margins, and even a few crossed-out words and numbers. Figure 2 is intended to reflect reality - how the completed pages will look and should look. The ACM-SADS is a working document, which will be completed by you in the field. Your goal in using the SADS is to communicate as much detailed information as possible about the ACM you are evaluating in a functional space. You should strive to record legibly everything which is pertinent to the ACM evaluation.

SECTION A PAGE

Begin completing the USA ACM-SADS by filling in the blanks in the general information section at the top of a section A page. Here are some additional guidelines for completing the form:

INSTALLATION

Write in the name of the installation or command whose facilities you are evaluating. Examples: Ft. Belvoir, USA-CERL

INSPECTOR

That's you, the person who is conducting the survey. Write in your first and last name and if you have one, your middle initial. The term "inspector" is used here rather than "evaluator" because it is important to emphasize that you need to be minimally an AHERA accredited inspector, to be qualified to conduct the survey and complete the survey pages of the SADS.

DATE OF INSPECTION

This is the date on which you complete the survey. If you start inspecting a functional space on one day and finish on another, record the date on which you were last inspecting the functional space.

AFFILIATION

If you are an Army employee, write in the name of your office, department, division, etc., or if you are an outside contractor, write in the name of the business or the firm you represent.

LOCATION INFORMATION

The purpose of the ACM survey is to locate, identify and measure the amount of ACM present in a functional space and in turn, a facility and the installation. In this part of the section A page you will begin providing the information which will precisely identify the location of a specific functional space and the ACM contained within.

FACILITY NO./DESCRIPTION

Basically, a facility is any structure designed and constructed to serve a specific function or perform a particular service and on which the Army spends money for upkeep. In most cases, from the standpoint of conducting an ACM survey, the facilities will be buildings. All facilities should have a number designation, which will appear on an installation map. In the blank provided on the section A page, write in the facility number and name or other description. In figure 2(a), you will note the inspector not only recorded the building number and its common name but included the comment that it is a two story structure.



FACILITY PURPOSE

Here you should write in terms such as: admin offices, school, storage, berthing, lodging, housing, maintenance, repair, etc.

DRAWING NO.

Write in the number(s) and date(s) of any as-built or other drawing(s) you have of the facility. If the drawing accurately shows the current condition or configuration of the facility, you may be able to write on it to indicate the boundaries you have selected for your functional spaces. The drawing would also be an excellent place to indicate the exact location of ACM in the space and where you have taken bulk samples and/or discovered damaged ACM.

FUNCTIONAL SPACE

Functional spaces are spatially distinct units or areas within a facility which are defined by walls or physical barriers and which may contain a population of workers, residents, other building occupants, or visitors. Examples of functional spaces are: offices, classrooms, corridors, janitor's closets, auditoriums, pipe chases, air shafts, air plenums, crawl spaces, boiler rooms, and even a stud wall. As the inspector, you define the functional space boundaries. If a functional space cannot normally be occupied, e.g., a stud wall, and it contains ACM, then you should list the ACM in the survey section B of the SADS but do not do an assessment. A unique number or code should be assigned to each functional space inspected. Existing identifiers, such as room numbers, are good to use and for other areas, simple codes may be devised. Record the number or code and a brief description of the functional space being inspected on the section A page and on any drawing showing the space.

SECTION A SURVEY-FUNCTIONAL SPACE CHARACTERISTICS

In this section, you will list special features of the functional space which can later be considered in the assessment of contained ACM, in the preparation of a special operations and maintenance program for managing any ACM in the space and/or for the planning of an abatement. Also, in this section you can make sketches or record information which better describe, define or characterize the functional space and any contained ACM.

(1) CEILING TYPE, HEIGHT AND SHAPE

Write in the type of ceiling and the height in feet, to the nearest foot, above the floor or ground level. The types of ceilings include: concrete, tile, metal deck, concrete joists and beams, corrugated steel, suspended metal lathe, suspended lay-in panels and steel beam or bar joists. In most cases, the shape of the ceiling in a functional space will be flat. In those cases where the ceiling of the space is also the roof of the facility, the other shapes listed may be applicable. Note that a pitched flat ceiling or roof is still considered flat. If the shape of the ceiling cannot be described adequately by the forms listed, you may check the "other" box and sketch the general shape or pattern of the ceiling.

(2) FLOORING TYPE

Write in one of the following, if it applies: concrete, ceramic or vinyl tile, brick, wood, carpet, earth. Otherwise, describe briefly the type of flooring.

(3) WALLS

Write in the number of walls in the functional space and the type of construction but NOT the surface covering. Examples are: 3-concrete brick, 2-poured concrete or 4-galvanized sheet

metal, referring to an air shaft as a functional space.

(4) LIGHTING TYPE/NO.

Record the type(s) of lighting you find in the functional space, e.g., surface, suspended or recessed and how many of each type are in the space. An example listing is shown in Figure 2(a).

(5) MACHINERY/EQUIPMENT

List here the types of machinery or equipment found in the space which may represent a significant source of vibration or brisk air movement, e.g., pumps, blowers, mixers, or for its use requires special access authorization, e.g., cryptographic gear, scientific-laboratory equipment.

(6) SKETCHES AND REMARKS

In Figure 2(a), line-item (6), you can see the inspector has drawn a fairly detailed drawing of the functional space, providing the location and brief description of all ACM and/or suspect ACM, the location of damaged ACM and where he took bulk samples for analysis. Dimensions of the space and other pertinent descriptive details have also been provided. This functional space does not appear on the 1953 as-built drawing of Bldg. 501 and therefore the inspector needed to provide the detailed drawing shown.

SECTION B PAGE

SECTION B SURVEY-ACM TYPE/QUANTITY

(7) TYPE OF ACM

Each of the six data columns in section B is used for one specific kind of ACM. The "kind" of ACM is defined by its type, function and form. The type of ACM will either be SM, TSI or MM and one of these codes should be written in a line-item (7) box for each kind of ACM you survey and list in the section B table. The codes for line-item (7) are listed along with the codes for line-items (8), (17) and (21) at the bottom of the page.

The ACM "type" is, of course, the column heading. You do not need to place the ACM type heading in any special order. In Figure 2(b), line-item (7), you will note the inspector arbitrarily placed surface materials in the first two columns, followed by the two thermal system insulations and lastly the miscellaneous material. In the sixth column, he listed another SM, perhaps because he forgot to list it along with the other two. It doesn't matter. The lineitem (7) entries could have been made as SM, TSI, SM, MM, TSI, SM, reflecting the order, perhaps, in which he discovered the ACM as he was inspecting the space. That order would still be acceptable. If the functional space contains more than six kinds of ACM, then you must use one or more additional section B pages to complete the survey. If the tailor shop, drawn in Figure 2(a), contained seven kinds of ACM, rather than just the six, the inspector would have included in the SADS another section B page, showing the seventh ACM listing. He then would have numbered the second section B page as "Page 3 of 13," if the ACM was undamaged, non-friable or "Page 3 of 15," if the ACM was friable or damaged, non-friable (friable or damaged, non-friable ACM would require another set of assessment pages, sections C and D).

(8) ACM FUNCTION/FORM

The next step in completing a column of survey information in the table is for you to assign a function/form letter-number combination to each specific ACM you are characterizing.

Under each ACM "type" column heading you list, fill in the appropriate line-item (8) box with one of the letters, A through K, and one of the numbers, 1 through 12, to indicate the function and form of the type of ACM. For example, if you were characterizing an ACM that was sprayed-on surface material, and which functioned as acoustical insulation, you would write the code, A7, in a line-item (8) box under a line-item (7) entry of SM. If you write in a function/form code which contains either the function-letter "K" or the form-number "12", you must provide a description of the ACM in the comments area on the page.

You will note in Figure 2(b), two of the line-item (8) entries have the same function-form code, i.e., B9. Although both ACM are the same kind, i.e., transite, the inspector considered the functional space's north-wall transite paneling different from the transite on the east wall. He therefore listed one of the transite homogeneous areas as B9-01 and the other as B9-02. Because the east-wall transite paneling was not damaged, the inspector took no bulk samples and therefore it may never be known if all the transite in the functional space is homogeneous.

Another common situation in which you will need to differentiate between two or more ACM of the same kind will be when you are surveying pipe insulation. You may have two or more lengths of F8 pipe insulation, which differ in lagging type or outside diameter but have the same asbestiform and asbestos percentage. For example, if three pipe runs had F8 insulation which differed only in the type of lagging, then you would list the three ACM as TSI, F8-01; TSI, F8-02; TSI, F8-03.

Once the line-item (7) and (8) boxes have been filled in with appropriate codes, a distinct column in the table has been established and you must enter additional data for one or more of the other line-items in the table to complete the column. For example, the column established by the SM, A7 codes, boxes in the same column and corresponding to line-items (9), (10), (11), (12), (13), (14), (19), (20), (21) and (22) may be required to be filled in with pertinent data. Likewise, a column established by the TSI, E6 codes may have boxes in the same column and corresponding to line-items (9), (10), (15), (16), (17), (18), (19), (20), (21) and (22) filled in with appropriate data.

Drawing upon your training and experience, you must identify in a functional space the different kinds of ACM. Keep in mind the AHERA concept of homogeneous areas. If a functional space has TSI consisting only of fifteen 2" steam lines, all insulated and lagged identically, and one 2" steam line insulated or lagged differently than the rest, then there are only two different function-forms of TSI ACM in the space.

(9) FRIABLE (Y/N)

Determine if each of the ACM in the functional space and listed in the table is friable. Record either a Y or N in the appropriate box. Remember, all friable and damaged, non-friable ACM must be assessed.

(10) LENGTH (FT-IN)

This line-item may apply to all kinds of ACM, but normally it should be used to record the length of TSI on pipes, ducts, shafts, etc. The measurements should be recorded to the nearest inch.

(11) WIDTH (FT-IN), (12) HEIGHT (FT-IN)

These line-items apply to both SM and MM. The measurements should be recorded to the nearest inch.

(13) DIAMETER (FT-IN)

This line-item may apply to all kinds of ACM, but you will usually use it to record to the

nearest inch the outside diameter of ACM insulation around cylindrical furnaces, boilers, and tanks.

(14) THICKNESS (IN)

This line-item may apply to all types of ACM. The thickness measurement should be recorded to the nearest eighth of an inch. The thickness measurement for the ACM, along with surface area measurements will allow the volume of ACM to be calculated. While the volume may not be important from an immediate health hazard standpoint (fiber release occurs at a surface), it will be an important measurement, if the ACM is to be removed.

(15) PIPE O.D. (IN)

Measure or estimate to the nearest quarter of an inch the outside diameter of all pipes in the functional space, which have ACM insulation. These measurements may be used to better characterize the functional space and later help identify homogeneous areas of ACM within the facility.

(16) PIPE ACM O.D. (IN)

Measure or estimate to the nearest half inch the outside diameter of all ACM pipe insulation.

(17) LAGGING TYPE

Lagging is the protective and confining jacket or covering placed over insulation. It protects the relatively soft, friable insulating material from mechanical abuse, supports insulating material which is subject to constant vibration and provides a smooth surface to be painted. Most lagging does not contain asbestos. Record the type of lagging as a code letter drawn from the list at the bottom of the table. CAUTION: The term lagging is used by some insulation workers to mean the covering and the insulation or the insulation itself.

(18) #FITTINGS/VALVES

This line-item will apply only to TSI types of ACM. Fittings are classified as branching, reducing, expanding, or deflecting. Fittings such as "tees," "crosses," "elbows," "reducers," "bushings," "couplings," and "unions" are commonly found in pipe runs, boiler connections and ductwork. Increasing the number of fittings and valves in any fluid network, increases the chances of leakage. If a steam line insulated with ACM has many fittings and valves, the leakage and/or maintenance/repair damage potential for the ACM is greater than for another steam line similarly insulated but with fewer valves and fittings. You should record the total number of fittings and valves for each TSI ACM using the following codes: Fittings (F) and valves (V) followed by a dash and the number of each, e.g., F-5, V-2.

(19) AREA (FT2)

The ACM in the functional space may be present in a shape, the surface area of which may not be easily determined from a set of a few measurements. If this is the case, you should do whatever measurements and calculations are necessary to determine the total ACM surface area. Record the result in the appropriate box of this line-item to the nearest tenth of a square foot. If you are not relying upon ASAPS to do the remaining area calculations, then you should also, using applicable length, height, width and diameter measurements, calculate and record here the surface areas for all the ACM listed in section(s) B.

(20) SAMPLE NOS.

You may use any form of sample number coding you wish, if you are not using ASAPS.



If you are using ASAPS, then you must restrict your codes to no more than 15 characters. As shown in Figure 2(b), the inspector, Albert S. Bestos, has used a 14 character code, in which the first 10 characters are his initials, ASB, the month, day and year of the inspection, and a dash. He has written the common "prefix" for his codes in the space available. The remaining 4 characters are a sequential number for a specific sample taken that day.

(21) ASBESTIFORM, (22) ASBESTOS%

If known to you at the time of your survey, record the type(s) of asbestos and percentage(s) by volume of asbestos in the ACM. For the asbestiform, use one or more of the code letters drawn from the list at the bottom of the table. If the asbestiform(s) and/or percentage(s) are unknown at the time of the survey, then the appropriate code(s) and value(s) can be entered later upon receipt of the sample analyses.

INSPECTED BY, DATE

Sign you name and record the date.

AHERA INSPECTOR ACCREDITATION NUMBER

Record your number. It may or may not have a letter prefix.

SOURCE AND MOST RECENT DATE OF ACCREDITATION

In most cases, your accreditation will have been issued by a state agency, in which case you should use the state's two letter code as the source. If your accreditation has not been issued by a state agency, briefly describe the source. In either case record the most recent date of accreditation.

SECTION C AND D PAGES

Whereas the survey documents the identity, location and quantity of <u>all</u> ACM, the assessment is only concerned with the friable and damaged, non-friable ACM. Line-items (23) through (28) in section C and (29) through (37) in section D are for the most part, self-explanatory. You should refer to Figures 2(a) through 2(l) and also the appendix of this technical manual for additional guidance on the completion of the assessment pages of the SADS. Remember, you must be an AHERA accredited Management Planner to assess ACM and complete the section C and D pages of the SADS. The signature block at the bottom of the section D page(s) should be completed in a manner analogous to the way it was done on the section B page(s).

Line-items (23), (24), (30) and (35) do require a few additional words of explanation. These line-items appear in the SADS as modified versions of the corresponding checklist assessment factors in the appendix. Line-items (23) and (24) show the additional ACM damage "conditions" of <u>Localized</u> and <u>Distributed</u>. If there is evidence of physical and/or water damage to the ACM you are evaluating, you should indicate in line-items (23) and (24) whether the damage is localized or distributed. These two conditions, if checked-off, contribute no points to the overall DAMAGE value for the ACM, but will be included as damage "qualifiers" in reports generated by ASAPS.

Line-item (30) has an additional assessment factor for pipe insulation. You are asked to indicate the total length of damaged insulation along the pipe run. If you cannot estimate the area of damaged pipe insulation, ASAPS will take your measurement of the total length of damage and multiply it by the circumference of the pipe insulation [derived from the O.D., line-item (16)] to calculate an area. ASAPS, of course, assumes that any damage to the pipe insulation, even a poke hole or gouge, involves the entire perimeter of the cylindrical insulation

along the length of damage. This usually does over-estimate the extent of damage, but it is an error on the side of caution.

Line-item (35) in the SADS shows an expanded set of conditions for Floor Surfaces-Special Situations. In the assessment checklist in the appendix, the evaluator is given the option of assigning a value of 1-4 points. In the SADS, you are asked to choose amongst the roughness conditions of High (4 pts.), Moderate (3 pts.), Low (2 pts.), Minimal (1 pt.) and Smooth (1 pt.).

Based upon points assigned (from the appendix) to the value-weighted conditions of lineitems in section C and D of the SADS, the total DAMAGE and EXPOSURE values and the corresponding assessment index have been determined for the ACM listed in Figure 2(b). These data are shown in the table below.

ACM TYPE, FUNCTION/FOR M	DAMAGE (D)	EXPOSURE (E)	ASSESSMENT INDEX
SM, B7	14	19	В
SM, B9-01	9	14	С
TSI, F8	17	17	Α
TSI, F4	7	12	С
MM, J11	7	10	7
SM, B9-02		NOT ASSESSED - MAGED, NON-FR	

Note: In each case, line-item (35) was valued at 4 pts.

US ARMY ACM SURVEY/ASSESSMENT DATA SHEET (ACM-SADS)

INSPECTOR: Albert S. Bestos INSTALLATION: Ft. Knight AFFILIATION: A.S. Bestos Consultants, Inc. DATE OF INSPECTION: LOCATION INFORMATION Facility No./Description: Bldg. 501 - Uniform Store & Warehouse (2-Story Structure)
Facility Purpose: Retail Sales, Storage Drawing No.: H653279 dtd. 05/12/53, As-Built Facility Purpose: Retail Sales, Storage Functional Space: RM 104 -(ground floor) Tailor Shop fitting rooms Survey - Functional Space Characteristics beams (sprayed-on ACM) Height (ft): 12 (1) Ceiling type: Concrete concrete Other (draw) ☐ Barrel ~ ☐ Folded plate ~ □ Dome / Yes, Height (ft.): I- beam (3) Walls: 2-concrete brick (2) Flooring type: 9" floor file, carpet 2- Stud walls (4) Lighting type/No.: Surface mounted (ceiling panel)-7, track lights (fitting RMS)-3 Light machinery, eig., Sewing machines, clothes press (5) Machinery/Equipment: loading dock Truck traffic to on driveway to (6) Sketches and remarks as appropriate to describe functional space. (Attach additional sheets if necessary.) Painted (89-01) Transite paneling WAREHOUSE AREA STEEL SUPPORT PILLAR CLOTHING RACK + STUD WALLS Œ OS STORAGE (HOM-LOAD BEARING) DO HOT APPEAR 20'-4" ON AS-BUILT DRING TO LOADING DOCK [89-02] 2" HOT WATER PIPE unpenhed TO 2ND FLOOR TOUSIE 6" ad ACM INSULAM CLOTH LAGGING - DAMAGED SEWING MACHINE AREA [F8] RETAIL (S) VAT 9" Vinyl Asbestos STORE THE (VAT) AREA WALL MOUNTED HYDRONIC HEATER DRIVEWAY FITTING (HOT WATER) ROOMS SERVICE (CARPETED COUNTER VAT ò CARPET OVER 14" HOT WATER PIRE. 5' DO ACH INSULATION METAL LAGGING WINDOW Bldg. Front 1' ABOVE FLOOR (D) = Damaged ACM (Location) TOTAL LOUGH 38 3 = Sample taken (Location) [F4] (ACM Costed) 4' a.c. run N-S over tailor shop (2 samples taken) [BT 5-Steel I-Beams

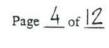


Facility No./Description	on Bldg	501	Funct	ional Space	Em 104 T	ailoz Shop
B Survey - ACM Ty	/pe/Quantity					1
(7) Type of ACM	SM	SM	TSI	TSI	ММ	SM
(8) ACM function/form	87	89-01	FB	F4	711	B9-02
(9) Friable (Y/N)	Y	N	Ÿ	T V	7	N
(10) Length (ft-in)			12-0	38-0	- 1	14-0
(11) Width (ft-in)		20-4		30 0		1,4-0
(12) Height (ft-in)		11-8				
(13) Diameter (ft-in)						
(14) Thickness (in)	1/2	3/8			//8	3/8
(15) Pipe O.D.(in)			2	1.5		70
(16) Pipe ACM O.D.(in)			6	5		
(17) Lagging type			Α	В		
(18) # Fittings/Valves			-	F-6, V-1		
(19) Area (ft²)	240		19		505	
(20) Sample Nos.	0047	0049	0051	0052	0054	
	0048	0050		0053		
100 10						
ASB 081590-						
(21) Asbestiform						
(22) Asbestos %	A, C	_ A	Α	C		
Comments:	60,10	S5	85	25		
No evidence of a paneling	encapsula [89-02]	tion on u	upainte	d trausite	1 Kess	ults not t available 8/30/90
Codes: 7) Type of ACM: Surfac	on Materials (C	M The 10		man	202	
7) Type of ACM: Surface 8) ACM Function/Form: (D) Potable water, (E) (I) Siding, (J) Flooring (5) Flexible sheet stoce (10) Other cementition	[Functions] [S Other cold line g, (K) Other; [F k-paper/millbo	SM] (A) Acoust es, (F) Other ho forms] (1) Loos ard, (6) Preform	tical insul. (B) of lines/steam. e-fill, (2) Blar	Struct fireproof, [MM] (G) Roofinket, (3) Thermal	TSI] (C) Thing, (H) Gaske	ermal insul, et seal,
17) Lagging Type: (A) C			per, (D) Cem	ent. (E) Board	(F) Other	
21) Asbestiforms: (A) Ch	rysorile, (B) Cr	ocidolite, (C) A	mosite, (D) T	Tremolite, (E) Ac	tinolite. (F) A	nthophyllite
	476	Soch	, ,	٨١, ــ, ١٨٠	1.	
INSPECTED BY	11.01	25/05		DATE 81	5/90	
		Accreditation N		4906 , I	98207	
Sour	ce And Most R	ecent Date Of	Accreditation	WI 5/10	88	



INSTALLATION: Ft. Knight MANAGE	EMENT PLANNER: A.S. Bestos
DATE OF ASSESSMENT: 815 90 AFFILIAT	TION: Bestos Consult
Facility No./Description Bldg 501 Functional Space: RM 104	ACM Function/Form:B7
C Friable ACM Assessment - Damage/Damage Potential	
(24) Water damage to ACM. Yes No	ACM debris on floor/work surfaces. None Localized Distributed Localized Distributed
B. Friable thermal system insulation [TSI]. Contamina Repair/maint. will damage ACM	eiling panel removal necessary and no repair/maint. ated ceiling panel removal necessary No damage likely
(28) Asbestos (%) content of ACM.	
Ceiling "I" beams Sprayed-on ACM debris on tops of drop ceiling panels. - Weekly practice at artillery rang space to rattle. - Noticeable vibration experienced in s west driveway. - hydronic (hot water) heating - nat insulated with fiberglass. Overall considued calm.	pace due to daily truck traffic

	lity No./Description Bldg 501 ctional Space: RM 104 ACM Function/Form: B7
run	ctional Space: KM 104 ACM Function/Form: B7
D	Friable ACM Assessment - Exposure Potential
(29)	Friability of ACM. High
(30)	Area of visible friable surface material or other damaged friable ACM.
	□ < 10 ft ² □ 10 ≤ ft ² < 100 ★ 100 ≤ ft ² < 1000 □ ≥ 1000 ft ²
	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).
	□ <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥ 50
(31)	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.
	□ Rough □ Pitted ★ Moderate □ Smooth
(32)	Ventilation: check all categories that apply.
	☐ ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airflow likely.
	☐ ACM in interior of return duct or plenum which is part of recirculating system.
	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainment potential.
	☐ None of the above apply.
(33)	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:
	☐ Turbulent air ☐ Moderate air streams ☑ Quiet air
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.
	☐ High (e.g., mechanical room) Med (e.g., forklifts, runway) ☐ Low (e.g., classroom, office)
(35)	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.
	Carpet or other difficult-to-clean material
	☐ Special (e.g., wood or dirt), roughness: ☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ Smooth
(36)	Barriers: ACM coverings.
	A. Surface Material (SM) on ceiling/walls.
	Suspended ceiling or accessible secondary wall
	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:
	□ ≤ 25% □ 25 < % ≤ 50 □ 50 < % ≤ 75 □ 75 < % ≤ 100
(37)	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.
	2 ≤ 9 or for corridors □ 10 ≤ pop ≤ 200 □ 201 ≤ pop ≤ 500 □ 501 ≤ pop ≤ 1000
	☐ ≥ 1001 or for medical facilities, youth centers, child care or residential facilities regardless of population
C	-1 1 5: 111
Λ	nents: 5 full time staff
14	relage 30 customers from outside bldg over an 8 hr. day. Each storner is serviced and gone within 15 min. (normally)
Cu	storner is serviced and gone within 15 min. (normally)
	30 cust. x 0.25 hrs. + 5 occupants = 6 persons (29)
	She Ac A Decision - 6 persons
EV	VALUATED BY: H. Destos DATE: 8/15/90
	AHERA Management Planner Accreditation Number MP 4906
	Source And Most Recent Date Of Accreditation WI 5/10/88





		ANAGEMENT PLANNER: A.S. Bestos
Fa	Facility No./Description Bldg 501 Functional Space: LM 104	ACM Function/Form: 89-01
c	Friable ACM Assessment - Damage/Damage Pote	ntiai
(23) (24) (25) (25) (26) (26) (28) (28)	Friable ACM Assessment - Damage/Damage Pote Physical damage to ACM. Rips, tears, gouges and/or evide High Moderate Low Minimal Water damage to ACM. Yes Proximity (P) of ACM to repair/routine maintenance areas. A. Friable surface material [SM]. P < 1 ft. or contam. 1 \leq P < 5 ft. P \geq 5 ft. P \geq B. Friable thermal system insulation [TSI]. Co. Repair/maint, will damage ACM Type of friable ACM: SM TSI MM Other non-friable ACM with exposed friable area: extended and proximity < 10 ft. High Med Low Asbestos (%) content of ACM. 1 < % \leq 30 30 < % \leq 50 \leq 6 > 50 Inments: Transite shows localized Acceptable area and pushed along a coat hanger of the transite has been so the pushed along a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the transite has been so the chips and Acceptable and a coat hanger of the chips and a coat hanger of the chips and Acceptable and a coat hanger of the chips and a coat hanger of the chips and Acceptable and a coat hanger of the chips and a coat hanger of the ch	Ince of ACM debris on floor/work surfaces. No Localized Distributed No Localized Distributed No Localized Distributed No Localized Distributed International panel removal necessary Soft. and no repair/maint. International panel removal necessary No damage likely No damage likely No damage likely Mod Low Min Maged friable ACM. Ignore barriers. (b) Proximity ≥ 10 ft. High Med Low All samples, no asbestos All samples, no asbestos All samples, no asbestos All samples, no asbestos All samples All samples All sam
	el e	

	Friability of ACM.			
	Area of visible friable surface material or other damaged friable ACM.			
	$\Box < 10 \text{ ft}^2$ $\Box 10 \le \text{ft}^2 < 100$ $\Box 100 \le \text{ft}^2 < 1000$ $\Box \ge 1000 \text{ ft}^2$			
F	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).			
	□ <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥50			
(31) V	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.			
	Rough Pitted Moderate Smooth			
(32) \	Ventilation: check all categories that apply.			
Section 1985	ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airfl likely.			
0	ACM in interior of return duct or plenum which is part of recirculating system.			
7	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainm potential.			
	None of the above apply.			
(33) A	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:			
	☐ Turbulent air ☐ Moderate air streams 🙀 Quiet air			
(34) A	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.			
0	☐ High (e.g., mechanical room) Med (e.g., forklifts, runway) ☐ Low (e.g., classroom, office			
(35) F	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.			
7	Carpet or other difficult-to-clean material Seamed or rough, hard surface Smooth, hard surface			
	Special (e.g., wood or dirt), roughness: A High A Moderate Low A Minimal Smooth			
(36) B	Barriers: ACM coverings.			
A	A. Surface Material (SM) on ceiling/walls.			
	☐ Suspended ceiling or accessible secondary wall ☐ Encapsulation ☐ Railing or wire mesh			
В	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:			
	$\square \le 25\%$ $\square 25 < \% \le 50$ $\square 50 < \% \le 75$ $\square 75 < \% \le 100$			
(37) P	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.			
2	≤ 9 or for corridors □ 10 ≤ pop ≤ 200 □ 201 ≤ pop ≤ 500 □ 501 ≤ pop ≤ 1000			
- 1	☐ ≥ 1001 or for medical facilities, youth centers, child care or residential facilities regardless of population			



cl	unctional Space: KM 104 ACM Function/Form: F8 Friable ACM Assessment - Damage/Damage Potential
_	Physical damage to ACM. Rips, tears, gouges and/or evidence of ACM debris on floor/work surfaces.
	☐ High Moderate ☐ Low ☐ Minimal ☐ None MacLocalized ☐ Distributed
24)	Water damage to ACM. ☐ Yes No ☐ Localized ☐ Distributed
25)	Proximity (P) of ACM to repair/routine maintenance areas.
	A. Friable surface material [SM]. P < 1 ft. or contaminated ceiling panel removal necessary
	☐ 1 ≤ P < 5 ft. ☐ P ≥ 5 ft. ☐ P ≥ 5 ft. and no repair/maint.
	B. Friable thermal system insulation [TSI]. Contaminated ceiling panel removal necessary
	Repair/maint. will damage ACM No damage likely
26)	Type of friable ACM:
	SM MM
	☐ Other non-friable ACM with exposed friable area: extent friable ☐ High ☐ Mod ☐ Low ☐ Mi
27)	Potential for occupant contact with friable SM or other damaged friable ACM. Ignore barriers.
	(a) Proximity < 10 ft. ☐ High Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ Low
28)	Asbestos (%) content of ACM.
	□ 1 < % ≤ 30 □ 30 < % ≤ 50
	Pipe insulation appears to have been damaged by a

D	Friable ACM Assessment - Exposure Potential
(29)	Friability of ACM. High
	Area of visible friable surface material or other damaged friable ACM.
	(10 ft^2) $(10 \text{ ft}^2 < 100)$ $(100 \text{ ft}^2 < 1000)$ $(100 \text{ ft}^2 < 1000)$ $(100 \text{ ft}^2 < 1000)$
	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).
	X <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥50
(31)	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.
	□ Rough □ Pitted ★ Moderate □ Smooth
(32)	Ventilation: check all categories that apply.
	☐ ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airflow likely.
	ACM in interior of return duct or plenum which is part of recirculating system.
	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainment potential.
	☐ None of the above apply.
33)	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:
	☐ Turbulent air ☐ Moderate air streams ☐ Quiet air
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.
	☐ High (e.g., mechanical room) Med (e.g., forklifts, runway) ☐ Low (e.g., classroom, office)
35)	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.
	Carpet or other difficult-to-clean material Seamed or rough, hard surface Smooth, hard surface
	☐ Special (e.g., wood or dirt), roughness: ☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ Smooth
36)	Barriers: ACM coverings.
	A. Surface Material (SM) on ceiling/walls.
	☐ Suspended ceiling or accessible secondary wall ☐ Encapsulation ☐ Railing or wire mesh ☐ Nor
	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:
SPIZEN.	$\triangle \le 25\%$ $\Box 25 < \% \le 50$ $\Box 50 < \% \le 75$ $\Box 75 < \% \le 100$
(37)	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.
	$\leq 9 \text{ or for corridors}$ $\Box 10 \leq \text{pop} \leq 200$ $\Box 201 \leq \text{pop} \leq 500$ $\Box 501 \leq \text{pop} \leq 1000$
	☐ ≥ 1001 or for medical facilities, youth centers, child care or residential facilities regardless of population



	acilia Na Magazinia (SI) a (N)
	unctional Space: RM 104 ACM Function/Form: F4
	Acti Function Politi.
eT.	Friable ACM Assessment - Damage/Damage Potential
_	Physical damage to ACM. Rips, tears, gouges and/or evidence of ACM debris on floor/work surfaces.
	☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ None ☐ Localized ☐ Distributed
24)	Water damage to ACM. ☐ Yes No ☐ Localized ☐ Distributed
25)	Proximity (P) of ACM to repair/routine maintenance areas.
	A. Friable surface material [SM]. Q P < 1 ft. or contaminated ceiling panel removal necessary
	☐ 1 ≤ P < 5 ft. ☐ P ≥ 5 ft. ☐ P ≥ 5 ft. and no repair/maint.
	B. Friable thermal system insulation [TSI]. Contaminated ceiling panel removal necessary
•	Repair/maint. will damage ACM
20)	Type of friable ACM: ☐ SM ☐ TSI ☐ MM
27)	The state of the s
	Potential for commant contact with frieble CM or other demand frieble ACM I
/	Potential for occupant contact with friable SM or other damaged friable ACM. Ignore barriers.
	(a) Proximity < 10 ft. ☐ High ☐ Med 🗡 Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L
	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM.
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:
28)	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L Asbestos (%) content of ACM. 1 < % ≤ 30 ☐ 30 < % ≤ 50 ☐ % > 50 ☐ All samples, no asbestos ments:

Fac	ility No./Description Bldg 501		
	ctional Space: KM 104	ACM Function/Form:	F4
	•		
D	Friable ACM Assessment - Exposure Potential		
		\ /	
	Friability of ACM.	□ Mod X Low	
(30)	Area of visible friable surface material or other damaged friable A		
		≥ 1000 ft ²	
	For pipe insulation, estimate the area and also indicate the total len	gth of the damaged section (s).	
-		25 ≤ ft < 50 ☐ ft ≥ 50	
(31)	Walls and horizontal surfaces; potential for ACM fiber entrapmen	t. Rate surface most difficult to clea	in.
	Rough Pitted Moderate Sm	ooth	
(32)	Ventilation: check all categories that apply.		
	ACM in interior of supply duct or plenum or within 5 ft. of supplikely.	ply diffuser/fan. Entrainment of fibe	ers into airflow
	ACM in interior of return duct or plenum which is part of recirc	rulating system.	1
	Air supply to room from (1) area of potential fiber release or (2) potential.) part of recirculating system with fil	ber entrainment
	☐ None of the above apply.		1
(33)	Air Movement in functional space which may affect ACM adverse	ly. ACM is subjected to:	1
N.VIII.	☐ Turbulent air ☐ Moderate air streams 💢 Qui	ALL LINE TO THE CONTRACT OF TH	1
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration		1
50 15.6	☐ High (e.g., mechanical room) Med (e.g., forklifts, ru		room office)
(35)	Floor surface - Refers to ease of removal of entrapped ACM fibers		osini onios,
	Carpet or other difficult-to-clean material Seamed or n Special (e.g., wood or dirt), roughness: High Modera	ough, hard surface Smooth	h, hard surface
(36)	Barriers: ACM coverings.	ate Low Minimal	□ Smooth
(30)	A. Surface Material (SM) on ceiling/walls.		1
		5	_
		apsulation Railing or wire m	nesh None
	B. Thermal System Insulation (TSI) or other friable damaged mater		
(27)		: % ≤ 75 □ 75 < % ≤ 100	1
(3/)	Population. Average occupancy and outside visitor traffic. Calcula		
		≤ 500 ☐ 501 ≤ pop ≤ 1000	
	☐ ≥ 1001 or for medical facilities, youth centers, child care or resid	lential facilities regardless of popula	tion
Comr	ments: ~ "exposed pipe		
	*11 + The end	Is of the insulation of	40
	Media organi	200 - 2	0-
	Quedasure Depo	ls of the insulation a sed - no skeet meta both ends of head	ta. (1-+
	lagging 5 T ancustre	born enas of new	ter (radiator)
EV	ALUATED BY:	DATE: 8/15/90	
	AHERA Management Planner Accreditation Number	1P4906 WI. 5/10/88	
		1 11-100	



F	unctional Space: M 104 ACM Function/Form:
C	Friable ACM Assessment - Damage/Damage Potential
(23)	Physical damage to ACM. Rips, tears, gouges and/or evidence of ACM debris on floor/work surfaces.
12710	High Moderate Low Minimal None Localized Distributed
in street	Water damage to ACM. ☐ Yes No ☐ Localized ☐ Distributed
(25)	Proximity (P) of ACM to repair/routine maintenance areas.
	A. Friable surface material [SM]. P < 1 ft. or contaminated ceiling panel removal necessary
	☐ 1 ≤ P < 5 ft. ☐ P ≥ 5 ft. ☐ P ≥ 5 ft. and no repair/maint.
	B. Friable thermal system insulation [TSI]. Contaminated ceiling panel removal necessary
	☐ Repair/maint. will damage ACM ☐ No damage likely
(26)	Type of friable ACM:
	□ SM □ TSI MM
	☐ Other non-friable ACM with exposed friable area: extent friable ☐ High ☐ Mod ☐ Low ☐ M
(27)	Potential for occupant contact with friable SM or other damaged friable ACM. Ignore barriers.
	(a) Proximity < 10 ft. ☐ High ☐ Med ☐ Low (b) Proximity ≥ 10 ft. ☐ High ☐ Med ☐ L
(28)	Asbestos (%) content of ACM.
	Asbestos (%) content of ACM. 1 < % \le 30 30 < % \le 50 \mathre{m} \rightarrow 50 \text{All samples, no asbestos} Not yet available 8/30/90
Comr	ments:
-	
	Small viens of horizon tile larm bonnak
	much frece of broken tire from beneath
	Small piece of broken tile from beneath clother press taken as sample for analysis
	clother press taken as sample for margus
	Tile mastic exposed
	Total Transition

D	Friable ACM Assessment - Exposure Potential
(29)	Friability of ACM.
	Area of visible friable surface material or other damaged friable ACM.
	\Box < 10 ft ² \Box 10 ≤ ft ² < 100 \Box 100 ≤ ft ² < 1000 \Box ≥ 1000 ft ²
1	For pipe insulation, estimate the area and also indicate the total length of the damaged section (s).
	□ <1ft □ 1≤ft<5 □ 5≤ft<25 □ 25≤ft<50 □ ft≥50
(31)	Walls and horizontal surfaces; potential for ACM fiber entrapment. Rate surface most difficult to clean.
	□ Rough □ Pitted Moderate □ Smooth
(32)	Ventilation: check all categories that apply.
	☐ ACM in interior of supply duct or plenum or within 5 ft. of supply diffuser/fan. Entrainment of fibers into airflow likely.
1	☐ ACM in interior of return duct or plenum which is part of recirculating system.
	Air supply to room from (1) area of potential fiber release or (2) part of recirculating system with fiber entrainme potential.
	☐ None of the above apply.
(33)	Air Movement in functional space which may affect ACM adversely. ACM is subjected to:
	☐ Turbulent air ☐ Moderate air streams ☐ Quiet air
(34)	Activity in functional space: Forces acting on ACM, e.g., vibration, water, steam.
	☐ High (e.g., mechanical room)
(35)	Floor surface - Refers to ease of removal of entrapped ACM fibers from floor. Check all that apply.
	Carpet or other difficult-to-clean material
	☐ Special (e.g., wood or dirt), roughness: ☐ High ☐ Moderate ☐ Low ☐ Minimal ☐ Smooth
(36)	Barriers: ACM coverings.
	A. Surface Material (SM) on ceiling/walls.
١	☐ Suspended ceiling or accessible secondary wall ☐ Encapsulation ☐ Railing or wire mesh ☐
	B. Thermal System Insulation (TSI) or other friable damaged material. % total exposed and visible:
	□ ≤ 25% □ 25 < % ≤ 50 □ 50 < % ≤ 75 □ 75 < % ≤ 100
(37)	Population. Average occupancy and outside visitor traffic. Calculate based upon 8 hr/day exposure.
1	△ ≤ 9 or for corridors □ 10 ≤ pop ≤ 200 □ 201 ≤ pop ≤ 500 □ 501 ≤ pop ≤ 1000
1	



APPENDIX

GUIDE FOR

ASBESTOS HAZARD ASSESSMENT

IN U.S. ARMY FACILITIES

1. Introduction

A survey is defined in this appendix as the inspection of functional spaces to locate, identify and measure the amount of ACM present. An assessment further evaluates the ACM in terms of (1) its potential to be airborne or the actual extent to which it is a source of fibers (damage), and (2) to what extent humans are exposed to airborne fibers in the functional spaces of a facility containing asbestos. Army asbestos management programs will include an assessment with any survey conducted.

The potential for fiber release and subsequent area contamination from ACM can be assessed by evaluating several factors, including the material's physical condition, characteristics, location and use. Information collected by assessing ACM in a functional space can be used to quantify the damage to the ACM and the occupants' asbestos fiber exposure potential and thereby produce an assessment index for the space. The asbestos management team can use the assessment index to compare functional spaces and ultimately prioritize the asbestos health hazards in a group of facilities.

The assessment algorithm presented and discussed in this appendix is self-contained and simple to use. The algorithm consists of an assessment checklist, an assessment index matrix and a table of recommended management actions. In accordance with AR 200-1, the assessment checklist must be completed by an AHERA accredited management planner. The management planner may use the checklist either in concert with a survey inspection of a functional space or in a separate evaluation of the ACM in a functional space at a later date, following a survey inspection.

11. Background

One of the first assessment techniques evaluated by the US Environmental Protection Agency (USEPA) was air monitoring. The idea was simple: air samples in the area around ACM would be collected to determine the concentration of asbestos fibers in fibers per cubic centimeter (f/cc). These concentrations could be compared with the Occupational Safety and Health Administration (OSHA) workplace standards to obtain a relative measure of the health hazard. Because air monitoring reflects conditions only at the time of sampling, it cannot serve as a measure of longterm fiber release potential. Air monitoring alone is not recommended by the USEPA for asbestos exposure assessment, nor is it used as part of any of the several commonly employed assessment schemes.

Many different assessment methods are currently available and are being used. All of the methods have the purpose and means of determining and documenting the conditions of ACM in a



functional space and what airborne asbestos fiber exposure potential exists for occupants of the space.

During the preparation of the assessment algorithm provided in this appendix, six assessment methods were evaluated:

- (1) EPA "Purple Book" Chapter 4
- (2) EPA Region VII 1982
- (3) EPA Draft 7 initial regulation 1986
- (4) US Navy TR883 Chapter 5
- (5) US Air Force "GRADE" system (based upon the Versar, Inc. method)
- (6) Hall-Kimbrell modified Sawyer algorithm.

Method 1 uses an empirical approach and method 3 is based on a "decision tree." Methods 2, 4, 5, and 6 are numerical rating schemes. Each of the methods has merit, is self-contained, and is designed to provide a relatively easy asbestos hazard assessment protocol.

In the 30 April 1987 issue of the Federal Register (52FR15820), the USEPA published a proposed rule under section 203 of Title II of the Toxic Substances Control Act concerning ACM in public and private schools. The background discussion states, "The negotiating committee generally agreed that assessment, as provided in the proposed regulation, should be flexible enough to accommodate a wide variety of acceptable and available methods and schemes. . . Assessment was perceived as the means of collecting and considering whatever data was necessary for the management planner to make an informed, responsible recommendation . . . consistent with response action requirements." The decision tree (method 3) in the USEPA initial regulation - Draft 7 (1986) was dropped due to committee sentiment that it was inappropriate for the USEPA to require a single assessment method.

In accordance with the current USEPA regulation governing asbestos abatement activities in schools, assessments of ACM hazards in schools must be performed by an accredited inspector, regardless of the assessment methodology used. The inspector shall gain his or her accreditation by attending a USEPA-approved 3 day training course and by passing an attendant examination. USEPA also suggests that states issuing the accreditation require the inspectors to have at least a high school diploma and perhaps an associate degree in appropriate fields (e.g., environmental or physical sciences). In light of this regulation, it is clear that the USEPA considers all assessment methods as tools to be used by or under the supervision of trained personnel.

As required by AR 200-1, ACM assessments must be completed by an AHERA accredited management planner. An accredited management planner has received additional ACM management training beyond his training for the inspector accreditation. This additional ACM

management training is considered necessary by the Army for the management planner to make the value judgements which are part of the assessment process.

III. Discussion

An asbestos hazards assessment scheme for the Army has to meet the following criteria:

- (1) Be easy to understand and use,
- (2) Be quantitative so as to provide a measure of hazard severity (assessment index) that will allow the Installation Commander to prioritize facilities in terms of the need for corrective action,
- (3) Provide a list of factors that cannot be easily quantified or included in an algorithm, but which the asbestos management team should consider in their decisions on corrective actions.

None of the six methods reviewed met all three criteria. The three USEPA methods were judged too empirical, providing an insufficient numerical basis for meaningful prioritizing. The modified Sawyer algorithm offered by Hall-Kimbrell and the Navy TR-833-Chapter 5 schemes failed to meet the third criterion. Although logical, the Air Force GRADE system with the multiple regression equation also failed to meet the third criterion. However, the assessment checklist in the GRADE system, which includes the factors concerning the ACM physical characteristics, condition, location, and use, is the most comprehensive of the six methodologies.

The assessment alogorithm discussed in this appendix is a modification of US Air Force "GRADE." The checklist (Figure 1a or 1b), differs in that it incorporates AHERA terminology but is otherwise similiar to the Air Force checklist. The multiple regression equation used in the Air Force Alogorithm has been replaced with an assessment index matrix, (Table 1). To use this scheme, a management planner works through the checklist making value judgments for each of the Damage/Damage Potential and Exposure Potential factors. A total numerical value for Damage and Exposure is derived which is then used in Table 1 to determine a letter assessment index. For each letter index, a recommended corrective management action is listed in Table 2.

The assessment algorithm is intended for use by a trained evaluator; that is, someone who is familiar with ACM and knows the layout and purposes of the buildings or facilities. The checklist applies to <u>friable</u> ACM or normally non-friable ACM which becomes friable as a result of damage. The ACM is also further classified as one of the three types; surface materials, thermal system insulation and miscellaneous materials. Other nonfriable forms of ACM shall be managed satisfactorily by an O&M program with abatement necessary only as part of facility alteration/repair, maintenance, or demolition.



An ACM Survey, locating, sampling, and measuring homogeneous areas of ACM should be conducted concurrently with the assessment when possible. The term "homogeneous area" refers to an area of surface material, thermal system insulation, or miscellaneous material that is uniform in color and texture.

IV. The Friable ACM Assessment Checklist

The Friable ACM Assessment Checklist is provided in a four-page annotated format (Figure 1a) and as a compact one-page format (Figure 1b). Both formats are fundamentally the same as those provided in method 5, but have several changes, primarily in terminology. The four-page format is intended principally as a training aid. As an evaluator becomes familiar with the assessment factors and what each of the value-weighted conditions means, he or she will be able to use the compact format.

The checklist is divided into two parts. Part I addresses the extent of existing damage and the potential risk of damage to friable ACM. Part II addresses exposure potential and the associated factors that contribute to health hazards in the occupied functional space being evaluated.

Evaluating the extent of damage to the ACM or the potential for damage is an important part of the assessment. This is because, in most cases, damaged ACM will release more airborne asbestos fibers than undamaged ACM under identical conditions. Also, the more extensive the damage, the greater the potential for fiber release.

Assessment factors, such as physical damage, water damage, asbestos content, and the attendent value-weighted conditions, in Part I of Figure 1a and 1b are self-explanatory. Other assessment factors, in Part I and II however, have additional considerations that could influence the evaluators choice of a value-weighted condition. The remainder of this section deals with some additional considerations.

The first assessment factor listed, in Part 1, Physical damage to ACM, has the five value-weighted conditions of high, moderate, low, minimal, and none. A consideration for the evaluator should be the age of the ACM. If the age is greater than 30 years, the normal deterioration of the binding agents may have produced a surface material that has a potential for fiber release, per unit of surface area damaged, much greater than for newer and similar surface ACM. An evaluator who would normally rate a certain extent of damage as "Low" for 15-year-old sprayed-on ACM might want to rate the same extent of damage as "Moderate" for a 35-year-old material. The age of the ACM should also be considered when assessing the potential for damage from water and routine maintenance or repair. In some assessment algorithms, the design of a roof above the ACM is considered. There is a greater potential for rainwater damage to ACM under a flat roof than under a sloped or hipped roof.

In considering the <u>Asbestos (%) content of ACM</u> factor, the assumption is that as the percentage of asbestos in the ACM increases so does the potential for airborne fiber release. This would undoubtedly be true if the same binding agent were used in all ACM. However, not all ACM are created equal. It is quite possible that an ACM with an easily degraded starch, water-soluble binder and an asbestos content of 15% would have a greater fiber release potential than an ACM with 50 percent asbestos and a water-insoluble binder.

The evaluator's choice of a value-weighted condition for each assessment factor should be based upon all specific and relevant information available.

V. Management Considerations

Even though an assessment index may accurately reflect the existing asbestos health hazard within a functional space, it probably will not be an accurate and complete measure of the asbestos management problem. The assessment index takes neither economic nor social factors into consideration. These factors often represent the greatest obstacles to managing and controlling asbestos hazards. A set of appropriate considerations is listed below.

A <u>Cost Considerations</u> (Estimating Cost Effectiveness)

- Cost of the abatement (contractor's estimate + in-house personnel dedication).
- 2. Cost of temporarily relocating personnel and equipment for the abatement.
- 3. Cost of nonproductivity resulting from relocation of personnel and equipment.
- Cost savings in preplanned remodeling, renovation and/or repair projects resulting from abatement activities.
- Cost savings associated with enhanced use of functional spaces, in facilities which have been purged of ACM hazards.

B. Morale Considerations

- 1. Effect on morale of abatement-related personnel relocation (see A-3)
- Effect of the notification of the need for abatement action on the morale of those individuals who occupy the space. Any abatement action will alert them to the fact that they had been working in a space determined as a high health risk environment.

C. <u>Miscellaneous Considerations</u>

- 1. Effects of flooding, wind, and fire damage on ACM integrity
- Climatological restrictions on abatements (Amended water can freeze, thus making spraying impossible!)
- Geographical restrictions on abatements (OCONUS facilities may have special problems)
- 4. Functional spaces which are controlled areas. Problems with (1) unauthorized access and potential compromise of classified materials in high security areas, (2) pilferage in warehouses, (3) existance of ignition sources (e.g., smoking, non-explosion proof electrical equipment) in or near



combustible material storage areas, associated with asbestos abatement workers.

Special facility use (child care centers and hospitals).

Figure 1a ARMY FRIABLE ACM ASSESSMENT CHECKLIST

Installation:	Management Planner:
Date of Assessment:	Affiliation:
Building No./Description:	
Functional Space:	
PART I: DAMA	AGE/DAMAGE POTENTIAL
surfaces. Score the friable ACM most exter (5) High - Dislodged pieces are evid (4) Moderate - There is evidence of (2) Low - Some evidence of material	dent on work surfaces. of visible material fallout. al fallout exists. d very small areas of material damage or fallout.
Water damage to ACM(3) Yes - Visible water damage(0) No - No water damage	
Proximity (P) of ACM to repair/rout apply, score the one with the highest rating	tine maintenance areas If both (a) and (b) g. (Check all that apply. Maximum of 3 points.)
(a). Friable surface material (SM): maintenance?(3) P< 1 ft or a ceiling panel contam(2) 1 ≤ P < 5 ft(1) P≥ 5 ft(0) ≥ 5 ft and no routine mainten	
(b). Friable thermal system insulation repair/routine maintenance? (3) Yes, and a ceiling panel contamination (1) Yes (0) No	n (TSI): Could damage occur as a result of nated with ACM must be removed.
Type of friable ACM If the functional spa friable material with the largest area. Che (4) Surface material (3) Thermal system insulation (TS (1) Miscellaneous material (MM)	
Other non-friable ACM with ((4) high(3) moderate(2) low(1) minimal	exposed friable area: extent friable



Potentia ACM fro	al for contact	t by occupant of the functional	s How far is t	the friable SM,	or other	damaged f	friable
exists?	(High, medium disturbing the	n, and low refer	to the chance	of the personn	el in the fu	inctional sp	oace

Proximity <10 ft(8) High(5) Medium(2) Low		Proximity ≥10 (5) Hig (3) Me (0) Lov	jh edium		
Asbestos (%) content of probability of becoming a(1) 1 < % ≤ 30(3) 30 < % ≤ 50(5) > 50 %All bulk samples from	airborne.				e highest NO HAZARD.
Bulk sample results (obta	ined from survey	data)			
Sample No.	Asbestiform	%	6	Source	
		Ev	valuated by:_		
DAMAGED (D) TOTAL	(Max 28 Min	1) 0	ato:		

ARMY FRIABLE ACM ASSESSMENT CHECKLIST Part II: EXPOSURE POTENTIAL

Friability of ACM Defined by USEPA: "Hand pressure can crumble, pulverize, or reduce to powder when dry." Score the friability of the SM or other damaged ACM with the largest area. (6) High - Material is fluffy and/or the slightest hand pressure can dislodge it. A slight breeze may disperse the material. (3) Moderate -Material can be dislodged or scraped or crumbled by hand. (1) Low -Material is firmly bound, difficult to scrape off by hand.
Area of visible surface material or other damaged friable ACM $(0) < 10 \text{ ft}^2$ (These small areas should be repaired ASAP). $(1) 10 \le \text{ft}^2 < 100$ $(2) 100 \le \text{ft}^2 < 1000$ $(3) \ge 1000 \text{ ft}^2$
Walls and horizontal surfaces; potential for ACM fiber entrapment Refers to the ability of the surface to hold ACM fibers for reentrainment. If more than one type of surface exists, score the roughest type or the most difficult to clean. If the material is exposed friable ACM(e.g. acoustical wall pannels), score as rough. ——(4) Rough - Difficult to clean with a HEPA vacuum. ——(3) Pitted - Difficult to clean with a damp cloth but cleanable with a HEPA vacuum. ——(2) Moderate - Can be cleaned with a damp cloth. ——(1) Smooth - Easily cleaned with a damp cloth.
 Ventilation Check all categories that apply. (Maximum 7 points) (5) The interior of the supply duct or plenum is coated or littered with friable material or is within 5 feet of a supply diffuser or fan and the condition of the ACM may cause fibers to be entrained into the airflow. (2) The interior of the return air duct or plenum is coated or littered with friable ACM and is part of a recirculating system. (1) Air being supplied to the room or area is: (1) drawn from an area where the potential for asbestos fiber release is possible, or (2) part of a recirculating system where fibers may be drawn into the system. (0) None of the above applies.
Air Movement in functional space which may affect ACM adversely (5) Material is subjected to routine turbulent or abrupt air movement. (2) Material is exposed to perceptible or occasional air streams. (0) No perceptible air flow exists in the functional space; quiet air.
Activity in functional space: Refers to forces acting on the ACM e.g., vibration, water, steam, etc. ——(5) High - Friable surface material or other damaged material is subject to constant vibration (ACM in a mechanical room). ——(2) Medium - Occasional vibration. (ACM in a warehouse where forklifts are used, next to an active runway, next to a kitchen) ——(0) Low - (ACM in an administrative office, library, classroom, storage room, stairway, corridor, etc. subject to minor or no forces effecting fiber release)



Floor surfaces: Refers to ease of removal of entrapped AC apply. (Maximum 4 points) (4) Carpet or an extremely rough surface difficult to cle cloth.	ean by HEPA vacuum or by a damp
(2) Seamed or rough surface (e.g., uncoated concrete). (1) Smooth continuous surface (e.g., finished or coated etc.).	d concrete, smoothly joined tile,
(1-4) Special situations (wood or dirt floors with vary	ing degrees of smoothness).
Barriers: ACM coverings: If both (a) and (b) apply, sco Check all that apply. (Maximum of 4 points)	ere the one with the highest rating.
 (a) Surface materials (SM) on ceiling or walls, are covered(1) Suspended ceiling or accessible secondary wall. (2) Encapsulation or covered with nonasbestos materi(3) Railing or wire mesh. (4) Nothing. 	
(b) Thermal system insulation (TSI) or other friable damaged exposed and visible to the occupants(1) ≤ 25%(2) 25 <% ≤ 50(3) 50 <% ≤ 75(4) 75 <% ≤ 100	d materials. Percent of total
Population. This involves defining the average occupancy a count visitors from within the building) of a functional space to For example, 15 individuals are normally assigned to the recepsee approximately 240 customers from outside the building over its serviced and gone within 30 minutes.	based on an 8 hr/day exposure.
([240 persons X 0.5 hours] / 8 hours) + 15 occupant	s = 30
Scor	re = 2
(1) \leq 9 or for corridors (2) 10 \leq Pop \leq 200 (3) 201 \leq Pop \leq 500 (4) 501 \leq Pop \leq 1000 (5) Pop \geq 1001 or for medical facilities, youth corresidential buildings, regardless of the population.	enters, child care facilities or
EXPOSURE (E) TOTAL(Max 43, Min 5)	Evaluated by:

Table 1 Determination of an Assessment Index

Each assessment factor in the checklist has one or more value-weighted conditions. For example, for the assessment factor, "Water damage to ACM," the value-weighted conditions are "Yes," valued at 3 points and "No," valued at zero points. For every value-weighted condition in the checklist, the corresponding point value, in parenthesis, follows a line, which is provided for the checkmark, used to indicate the assessment factor condition selected by the evaluator. Following the selection of value-weighted conditions for all assessment factors in Part I of the checklist, the sum of the points is determined. This sum is the DAMAGE value, entered at the end of Part I and is used in the matrix below. The EXPOSURE value is similarly determined from data in Part II and used as the second entering argument in the matrix.

Using the Damage/Damage Potential and Exposure Potential values derived from the checklist (Figure 1a or 1b), as entering arguments, use the matrix below to find the corresponding assessment index.

		Exposure $(4 \le E \le 43)$			
		43-26	25-17	16-8	7 - 4
Domono	28-17	Α	Α	Α	В
Damage $(1 \le D \le 28)$	16-11	Α	В	С	D
	10-5	Α	В	С	E
	4-1	Α	С	D	F

Table 2 Assessment Index Recommended Management Corrective Actions Α Immediate Action - Requires further assessment by accredited personnel* (in-house or contractor) who are experienced and qualified to conduct asbestos assessments. Possible follow-up actions may include isolating the area, restricting access, and/or removing the necessary ACM immediately. If removal is immediate a detailed survey should be conducted. This action will likely involve a near term expenditure of funds. Managers must know exactly what needs to be done to eliminate the asbestos hazards and how to use available funds most effectively. В Action as Soon as Possible - Requires further assessment by accredited personnel* (in-house or contractor) who are experienced and qualified to conduct asbestos assessments. Initiate a Special O & M** program immediately. Possible follow-up actions may include the limiting of access to the area and the scheduling of removal during periods of low activity in the facility, not waiting for the normal repair and maintenance cycle. C Planned Action - Requires further assessment by accredited personnel* (in-house or contractor) who are experienced and qualified to conduct asbestos assessments. Initiate a Special O & M** program. Removal should be scheduled as part of the normal repair and maintenance cycle of a facility, minimizing cost and disturbance. Repair - Initiate Special O & M** using accredited personnel*. D Damaged areas should be repaired, where "repair" means returning damaged ACM to an undamaged condition or to an intact state so as to contain fiber release. Schedule removal when practical and cost effective. Take preventative measures to reduce further damage. E

Monitoring - Continue Special O & M** using accredited personnel*. Take steps to prevent damage to the ACM. Monitor frequently the condition of all ACM.

No Immediate Action - Continue Special O & M** using accredited personnel* until major renovation or demolition requires removal or until assessment factors change.

*Accredited personnel are industrial hygienists (certified by the American Board of Industrial Hygiene [ABIH] or qualified according to the Office of Personnel Management's 0690 classification standard) and other trained persons with a minimum of 1 year experience in asbestos assessment activities who are accredited in the specific area for which they are responsible (e.g., inspector-management planner, abatement designer, contractor, supervisor, and abatement worker) as specified in Section 206 of Title II of TSCA.

** An O & M program may include enclosure and encapsulation, where appropriate, to increase

effectiveness.

F

DESTRUCTION OF EXPLOSIVES AND ROCKET FUELS BY SUPERCRITICAL WATER OXIDATION

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ABSTRACT

The destruction of energetic materials, including propellants, explosives and pyrotechnics (PEPs) by oxidation in supercritical water is described. The focus is on the chemistry of the process. The destruction efficiencies and products of reaction contained in the aqueous and gaseous effluents of several representative PEPs are reported.

INTRODUCTION

Traditional methods for disposing of PEPs have been open burning or open detonation (OB/OD); however, regulatory agencies are likely to prohibit OB/OD because of the uncontrolled air emissions and soil contaminations. Likewise, controlled incineration carries a liability for air pollution because large quantities of NO_X are produced in the conventional combustion chemistry of PEPs. Soil and ground water have already been contaminated with PEPs through normal operations at manufacturing plants and military bases. Incineration can be used for decontamination of these soils, with the associated liability for air pollution, but few satisfactory and economic methods exist for ground water decontamination. A clear need exists for improved disposal and destruction methods.

The principle of supercritical water oxidation (SCWO) has been successfully demonstrated. High destruction and removal efficiencies (DREs) have been reported for a broad range of common solid and liquid wastes, including difficult examples such as chlorinated aromatic solvents. These same studies have indicated that the major reaction products were water, carbon dioxide, and inorganic salts. The general approach is to mix the waste with an oxidant (oxygen, air, or hydrogen peroxide) in water at pressures and temperatures above the critical point (374 °C and 22.13 MPa). Under these conditions, water is a fluid with densities high enough that reasonable process throughput can be achieved, but its transport properties are like those of a gas, allowing rapid chemical reaction. Supercritical water (SCW) is a unique solvent medium in which oxidation can take place at lower temperatures than incineration, thus limiting the production of NO_x and char. The reaction is entirely enclosed in a pressure vessel at concentrations low enough that the heat of reaction is absorbed by the solvent. As a result the temperature can be maintained at any desired level (typically in the range 400-650 °C). Oxidation occurs rapidly, on the time scale of seconds to minutes, and produces simple products (ideally CO₂, H₂O, and N₂).

A great range of scale appears to be possible for supercritical water oxidation plants. Standard pressure-vessel technology can be used to provide small mobile units or permanent medium-sized surface installations for processing of laboratory or manufacturing wastes. Plants with very large

capacities have also been proposed, in which a cylindrical heat exchanger and reaction vessel are placed in the ground by use of oil-field drilling and well-completion technology. Operation of a SCWO unit for the treatment of explosive wastes would need to be controlled remotely. The details for full scale operation (site preparation, facility needs, utilities) will depend on the waste being treated and the particular design of the reactor (i.e., tube, vessel, in-ground, etc.). A more complete description of the operation of full-scale SCWO units, including materials throughput, mass balances, and equipment design, can be found in several reports.⁴

Compared to other available technologies, supercritical water oxidation is applicable to a broader range of waste types. It can be used to treat pure organics, contaminated soils and water, sludges, and some inorganics. At present, public concern should not delay obtaining operating permits. The complexity of the technology is comparable to incineration so that with proper engineering and process controls, qualified technicians should be able to be operate and maintain an SCWO unit.

Incineration is a non-specific alternate method for destroying organic materials. Incineration can be operated at a relatively low cost, but requirements for extensive emission controls and difficulties associated with obtaining permits can negate potential advantages. Supercritical water oxidation takes place at a much lower temperature (about 500 °C) than incineration and in a completely contained system. Almost no oxides of nitrogen are expected at these low temperatures, and the effluent is completely contained and controlled. Supercritical water oxidation can be applied to water containing 20% or less organic waste. By comparison, incineration is not as cost effective at these concentrations. Cost estimates for developing technologies, such as SCWO at full scale, are inherently uncertain and should be considered cautiously. The cost of SCWO of wastes has been estimated in several studies.3,4 For treating a ton of dry organic material, the costs are estimated to be between \$300 and \$600 per ton depending on the size of the SCWO treatment unit.⁴ Other methods under development that may apply to explosive wastes include oxidation by hydrogen peroxide and/or ozone with UV radiation, electrochemical oxidation, and oxidation in molten salts. In two-phase systems such as these, concentration gradients across phase boundaries and mass transfer of oxygen limit the rate and extent to which compounds can be completely destroyed. A supercritical fluid is single phase making complete mixing possible; thus, reaction rates are not diffusion limited. A preliminary cost comparison of these oxidation processes prepared by the Energy and Environmental Analysis Group at Los Alamos National Laboratory estimates the costs for the UV processes for contaminated water are 10 to 100 times less per gallon of water than for SCWO. However, these technologies are limited to low (<1000 ppm) organic concentrations. Concentrated wastes would need to be diluted. In addition, these methods usually require special pretreatment of the waste water, thereby increasing costs.

The Environmental Protection Agency (EPA) has informally stated that supercritical water oxidation is not considered to be incineration, thus it will probably be permitted under Part X. If supercritical water oxidation units become an integral part of a manufacturing process, the EPA will not consider the unit to be a treatment facility, implying that waste water and air discharge permits are sufficient. In a demonstration of SCWO technology in New York State, the MODAR corporation obtained a permit under the New York State Environmental Conservation Law, and approval from the EPA to treat polychlorinated biphenyls (PCBs). The waste analysis plan and trial test plan were developed to comply with the Resource Conservation and Recovery Act (RCRA) regulations. A second demonstration by MODAR at a chemical plant in Pennsylvania did not require similar permits since PCBs were not being treated and the effluent was sent to the plant's water treatment facility.

This work seeks to examine the behavior of energetic substrates, including Ammonium perchlorate (AP), Cyclotrimethylene trinitramine (RDX), Cyclotetramethylene tetranitramine (HMX), Nitroguanidine (NQ), Nitromethane (NM) Pentaerythritol tetranitrate (PETN) and 2,4,6-Trinitrotoluene (TNT) under conditions of SCWO to provide the DREs of the substrates, to

determine the optimum conditions for maximizing the DREs, and to ensure safe operation. Products of destruction are identified and measured. Experimental results are evaluated to determine whether the reaction products are environmentally acceptable. Corrosion studies are underway to determine the suitability of various reactor materials. In addition, safety studies are in progress to determine the detonation sensitivity characteristics of PEPs in supercritical water systems.

EXPERIMENTAL APPROACH

This section describes the reactors used to destroy high energy materials through SCWO processes, and the analytical methods used to measure product species. The specific experimental conditions under which the destruction measurements were performed will be presented in the results and discussion section.

Bench-scale linear flow reactors have been developed to destroy explosives in supercritical water. A schematic of a linear flow reactor is shown in Figure 1. Solutions of oxidizer and/or explosive are introduced at high pressure into the reactor by constant flow, high performance liquid chromatography pumps (LDC Analytical, Constametric 3200). The explosives are typically in water at less than half their solubility limit or decomposed in water as the result of prior hydrolysis reactions. Check valves are placed in each line to prevent back streaming in case of pump failure. Fuel and oxidizer are either premixed before being pumped or are introduced separately. In either case, mixing is completed before reaching the heated section of the reactor. The central core of the reactor is heated to a controlled temperature by six heaters in parallel consisting of hollow brass tubes wrapped with MgO2 insulated nichrome wire. The temperature is maintained by regulating the current through the heating wire with Omega CN9000 series microprocessor temperature controllers. The temperature of each of these heaters can be varied independently; however, for all experiments described in this report the temperature of each heated section was kept the same. The temperature is monitored with six K-type (chromel-nickel), sheathed thermocouples in close proximity to the reactor core. A water-cooled heat exchanger at the exit cools the reacted mixture to room temperature. The cooled effluent is passed through a 7 µm filter for removal of any particulate matter before reducing the pressure to ambient with a let-down valve. Gas and liquid effluents at ambient temperature and pressure then enter a gas-liquid separator.

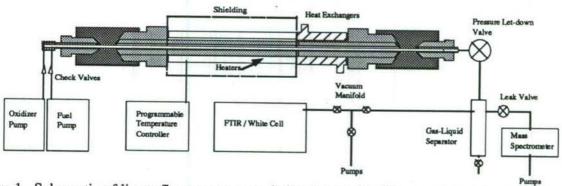


Figure 1. Schematic of linear flow reactor coupled to the gas-liquid separator and pumping manifold and pathways to various gaseous analysis.

The high temperature portion of one of our linear reactors is constructed out of C-276, a nickel alloy. The C-276 alloy was chosen because of its known strength and resistance to corrosion at high temperatures. Even so, under some reaction conditions we have seen considerable corrosion. To overcome this problem, a second reactor was constructed containing a 316 stainless steel sheath with a gold liner. A seal was made with the gold liner by flaring one end of the gold tube and compressing it between tapered high pressure fittings. The liner is open at the exit of the reactor,

creating a static supercritical region between the liner and stainless core. The gold liner protects all high temperature sections of the reactor. All "taper seal" high pressure fittings, and most other components obtained from High Pressure Equipment Co., are manufactured from 316 stainless steel and rated to a minimum of 4080 atm. The C-276 reactor core is 64 inches long by 0.083 in. inside diameter (id), and the gold-lined stainless steel reactor is 55 in. x 0.103 in. These dimensions provide a heated volume of 5.7 ml and 7.4 ml, respectively. Using an empirical equation of state for supercritical water⁵ we estimate a residence time of 5-150 seconds, depending on flow rate (typically 1-8 grams/min) and temperature (400-600 °C) with a pressure of 340 atm.

We have developed a variety of analytical approaches to quantifying residual energetics and products of reaction in the aqueous and gaseous reactor effluents. The gaseous effluent is primarily analyzed using Fourier-Transform Infrared (FTIR) Spectroscopy. A procedure was developed to quantify the concentration of CO2 and N2O (the primary gas phase products) produced using a 1 m path length cell. Calibration curves for CO2 and N2O were obtained by measuring the fraction of infrared light absorbed by a series of known concentrations of CO2 or N2O in the range expected to be produced in SCWO reactions. The dependence on concentration of the integrated absorbance of each of the two major CO2 IR absorptions (asymmetric OCO stretch, 2350 cm⁻¹ and OCO bend, 630 cm⁻¹) was nonlinear, exhibiting distinctive saturation behavior over the range of pressures (concentrations) from 0.1 to 10 torr, a consequence of the narrow linewidths of the ro-vibrational line and the limited (0.5 cm⁻¹) resolution of the FTIR. The resulting calibration data were fit to a saturation function, y=a(1-e-bp)+cP where P is the partial pressure of the absorbing gas. This technique enabled us to measure the gas pressure with a relative standard deviation of 3%. A UTI quadrupole mass spectrometer is also used for detection of H2, N2, and O2. Gaseous products are sampled on-line through a leak valve. To obtain a steady leak rate, a constant backing pressure of sample plus He buffer gas (600 torr total) was maintained. The pressure in the quadrupole region was typically in the 10-5 torr range. Calibration of this technique has so far proved difficult due to constantly changing backgrounds.

Analyses in the liquid phase included metals, total organic carbon (TOC), total inorganic carbon (TIC), inorganic anions and the substrate energetics. Metals analyses for Cr, Ni, Fe, Mo and Au are performed on a Perkin-Elmer inductively coupled plasma spectrophotometer (ICP) using indium as an internal standard. Total organic carbon (TOC) and total inorganic carbon (TIC) are analyzed using a Rosemount Dohrmann Model DC-190 Carbon Analyzer. Calibrations are performed with each set of samples using different concentrations of standardized potassium acid phthalate solution. Inorganic anions, particularly nitrate, nitrite and chloride, are analyzed with a Dionex 4500i Series Ion Chromatograph using a Dionex IonPac AS4A column with an eluent consisting of 1.5 mM NaHCO3 and 2.2 mM Na2CO3. In most cases conductivity detection is used, but a UV/Visible detector set at 215 nm is used for low levels of nitrate and nitrite. Trace amounts of TNT, PETN, HMX, NQ, and RDX are analyzed by reverse phase liquid chromatography on the Dionex 4500i. The liquid chromatograph uses a Waters 490E Programmable Multiwavelength Detector that allows for simultaneous, multiwavelength detection. This feature is particularly useful if interferences are present, since interferences usually give different signals at different wavelengths. All these compounds are analyzed using a 150 mm x 2.1 mm id Č8 narrow-bore column that is slightly heated for temperature stability.

RESULTS AND DISCUSSION

SCWO Reactions of energetics below solubility limits. Most of our effort has focused on reactions of solutions having concentrations less than half of their room temperature solubilities. The destruction efficiencies for the SCWO of five explosive compounds, PETN, HMX, RDX, TNT, and NQ are given in Table I. These reactions were run at high temperatures (near 600 °C) and with a large excess of oxidant.



TABLE I. Destruction Efficiencies for Energetics Below Water Solubility Limits^a

Substrate	PETN	HMX	RDX	TNT	NO
Initial conc. (ppm)	3.8	2.6	35.2	65.5	1700.
Destruction efficiency	>0.9825	>0.9900	>0.9992	>0.9998	>0.9999

aConditions: 600 °C, 5500 psi; excess H₂O₂; 11 s residence time; gold-lined reactor.

The initial concentrations of the explosives were kept at less than half their room temperature solubilities to prevent precipitation and accumulation of explosive material in the feed lines leading to the reactor. Hydrogen peroxide was used as the oxidizer and was mixed with the feedstock containing explosives before the fluids were heated. In all cases the oxidizer was in 30-fold excess of the stoichiometry required to convert the explosive to CO2, H2O and N2. The experimental conditions for each of these explosives were nearly identical, with pressures of 340 atm, reactor temperatures of 600 °C and residence times of 11 seconds. The reactions were primarily run in the gold-lined reactor to minimize the heterogeneous chemistry that might occur at the reactor walls. The only compound for which any reactor dependent chemistry has been observed is AP. No significant difference in DREs and products chemistry was observed for reactions of TNT, HMX, and RDX in the C-276 and the gold-lined reactors. We conclude from these observations that reactions with the C-276 and stainless 316 walls must not be significant for these energetic materials. For these "extreme" conditions, the aqueous effluent contained no detectable amounts of explosives. The detection limit of the HPLC/UV-vis analysis ranges from 20 to 50 parts per billion (ppb) depending on the compound. Consequently the measured destruction efficiencies represent lower limits defined by the low starting concentrations and the detection limits.

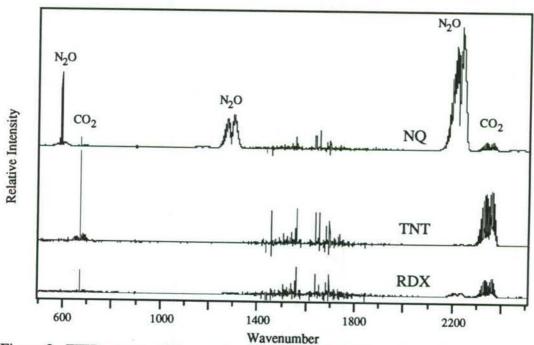


Figure 2. FTIR spectra of the reaction products of SCWO of TNT, NQ and RDX.

Gaseous and liquid effluents from these reactions have been analyzed to determine the products of reaction. Typical FTIR spectra for TNT, NQ and RDX are shown in Figure 2. It is clear from these analyses that the extreme conditions of high temperature and excess oxidant produce only CO₂ and N₂O in the gaseous effluent. Other possible products such as CO, CH₄, NO and NO₂

are not detected and are therefore below parts per million (ppm) levels (generally below 0.1% of the starting C and N). Additional products that are likely to be produced in these reactions but which cannot be quantified by FTIR include N₂, O₂ (no infrared active vibrations) and H₂O (swamped by large water background absorption).

The reactor effluents have been analyzed for carbon content and the results are summarized in Table II. The final two columns list the percentage of the starting C that is observed in the aqueous effluent (as organic and inorganic C) and as CO₂ in the gaseous effluent. For PETN and HMX, both the TIC and TOC quantities are below detection limits (0.1 ppm). Detectable quantities of organic carbon were found for RDX, TNT and NQ. Since in all of these cases the substrate is destroyed to levels well below the detection limits of the HPLC analysis (10 ppb) and since no volatile organics were observed in the FTIR analyses, the observed organics must be nonvolatile reaction products such as formate or acetate. For the TNT reactions, greater than 98% of the C was detected as CO₂, with the remainder detected as involatile organics in solution. The only substrate to give significant TIC (carbonate or bicarbonate) quantities is NQ. In this case, 83% of the C is detected as CO₃²⁻ or HCO₃⁻ while 15% is detected as gaseous CO₂, accounting for most of the C.

TABLE II. Analysis of Carbon Products in Effluent Streams for SCWO of Energetics^a

Substrate	[C] _i ^b (ppm)	TIC (ppm)c	TOC (ppm)c	% Caqueous	% C _{CO2}
PETN	2	d	d	d	81
HMX	2	d	d	d	87
TNT	24	0.2	1.7	8	98
RDX	5.7	< 0.1	< 0.1	<4	98
NQ	195	152	10	83	21

^aConditions: 600 °C, 5500 psi; excess H₂O₂; 11 s residence time; gold-lined reactor; ^bInitial carbon concentration.; ^cTIC, Total inorganic carbon, TOC, Total organic carbon; ^dSince starting concentrations of PETN and HMX are ~2-3ppm, the analyses for TOC and TIC are below detectable limits;

Reactor effluents have also been analyzed for nitrogen content and the results are summarized in Table III. For PETN, HMX, and RDX, some N_2O was observed in the FTIR spectra, but quantitative analysis showed the amounts to be less than 0.5% of the initial N. With excess oxidant, significant amounts of nitrite and nitrate were observed for all substrates except NQ. Most of the detected N from NQ was determined to be N_2O . Trinitrotoluene (TNT) produced the greatest fraction (65%) of NO_x^- .

TABLE III. Analysis of Nitrogen Products in Effluent Streams for SCWO of Energetics^a

Substrate	PETN	HMX	RDX	TNT	NQ
% NO ₃ -	18.7	12.4	10.1	36.6	0.03
% NO ₂ -	6.0	5.3	14.1	28.5	0.04
% N ₂ O	b	b	b	4.0	35

^aConditions: 600 °C, 5500 psi; excess H₂O₂; 11 s residence time; gold-lined reactor. ^bLess than 0.5%.

In all cases examined so far, a large fraction of the initial nitrogen remains undetected by our current analytical techniques. We have recently interfaced a mass spectrometer to the gas-liquid separator on the gold-lined reactor which enables us to obtain on-line analyses of the effluent gases. We have observed formation of N₂ in the SCWO oxidation of TNT. However, we have not yet worked out the calibration protocol for making these analyses quantitative.

Effects of temperatue and oxidant concentration on SCWO of TNT. A large number of experiments has been conducted on TNT to determine the SCWO chemistry as a function of reaction temperature and oxidant concentration. In all cases, the TNT was destroyed to below detectable limits of ~10 ppb, yielding a destruction efficiency of greater than 99.98%. product analysis results are summarized in Table IV. The NO2- and NO3- values are listed as a percentage of the starting nitrogen concentration. Similarly, the TIC and TOC values are listed as a percentage of the starting carbon concentration. The ratio of H2O2 to TNT represents a stoichiometric ratio based on complete reaction of TNT with H2O2 to form CO2, H2O, and N2. The most efficient conversion of TNT to CO2, as determined by FTIR analysis of the gas production and by the TIC and TOC analyses of the aqueous effluents, occurs at the highest temperature (600 °C) and the highest H2O2 concentration. These conditions also yielded the highest concentrations of NO₂- and NO₃-. In general, at lower temperatures and lower ratios of H₂O₂:TNT, less NO₂ and NO₃ are observed. While these conditions do not compromise the destruction efficiency of TNT, they tend to leave more carbon in the aqueous effluent. Much of this carbon appears as carbonate, however, which can be removed by lowering the pH. The best conditions for the destruction of TNT and any organic byproducts with minimum NO2- and NO3formation appear to be 600 °C and a 1:1 stoichiometric ratio of H2O2:TNT.

TABLE IV: TNT SCWO products as a function of temperature and H₂O₂ concentration

Temp (°C)	H ₂ O ₂ :TNT ^a	%NO ₂ -	%NO ₃ -	Total %NO _x -	%TIC	%TOC	%Total
400	20:1	11	30	41	4	18	22
500	0:1	18	0	18	14	28	42
500	20:1	26	51	77	4	11	15
600	0:1	18	0	18	12	34	46
600	1:1	11	6	17	15	0	15
600	2:1	6	6	12	14	0	14
600	5:1	33	38	71	9	0	9
600	20:1	25	49	74	4	0	4

^aStoichiometric ratio

Reactions of Ammonium Perchlorate (AP). The chemistry of AP is unique and consequently is discussed separately. Because of corrosion problems, most AP SCWO reactions were performed in the gold-lined reactor. Some results in the C-276 reactor are included for comparison. Sodium hydroxide was always added to the AP solutions in a 1:1 stoichiometry to ensure a net pH balance. This is particularly important for the gold-lined reactor, where the presence of a high Cl⁻ ion concentration together with a low pH and highly oxidizing conditions may result in the oxidation of the gold liner to AuCl4⁻.

Data for the dependence of destruction efficiencies and reaction products on temperature are summarized in Table V. The products containing Cl and N are given as a percentage of the initial Cl and N concentration, respectively. At temperatures lower than 400 °C, no decomposition of the ammonium perchlorate is observed. Most of the ammonia and all the perchlorate are recovered. The small ammonia loss is most likely due to the evolution of ammonia gas from the feed solution and effluent. The AP begins to react at 450 °C and is completely destroyed (99.6%) at 600 °C. Almost all the chlorine from the perchlorate appears in the effluent as sodium chloride (NaCl). Although salt solubility decreases in supercritical water, the sodium chloride product remains in solution at low concentrations or temperatures. However, when the concentration and/or temperature are raised, the Cl mass balance is degraded, probably due to precipitation of Cl-salts in the reactor. We have found that our mass balances improve when the reactor is cooled and flushed

between runs and the 'flush' solutions are included in the analysis. With this procedure a burst of Cl⁻ is generally observed in the first or second flush sample as the reactor is cooled. The liquid effluent also contains a small amount (<2%) of nitrogen as nitrite (NO₂⁻) and nitrate (NO₃⁻). The mass spectra indicated that both nitrous oxide (N₂O) and oxygen (O₂) are produced. The amount of N₂O produced was quantified using the FTIR/White cell and appears to increase with increasing temperature and AP concentration. Most of the N was not detected (for the best case, 600 °C, only 25% is detected) and likely occurs as N₂. The FTIR and mass spectrometric analyses of the gaseous effluent did not detect the presence of chlorine (Cl₂), nitrosyl chloride (NOCl), or nitrogen dioxide (NO₂).

TABLE V. AP SCWO Products as a Function of Temperature^a

T (°C)	% ClO ₄ -	% Cl-	% NO ₂ -	% NO ₃ -	% N ₂ O	%NH ₄ +
400	100	0.0	0.3	0.0	0.0	95.0
450	95.5	6.9	0.8	0.3	1.3	85
500	46.0	16.0	0.0	2.0	13.6	40.0
550	3.5	17.0	0.0	2.0	23.1	0.0
600	0.4	5.0	0.2	0.2	23.3	0.0

^aConditions: 0.1 M AP; equimolar NaOH; residence time varied from 11 - 52 s (600 - 400 °C); flush between runs not analyzed; gold-lined reactor.

Previous studies of the thermal decomposition of solid ammonium perchlorate show that a variety of products is possible.⁶ Below 300 °C, the equation

$$4 \text{ NH}_4\text{ClO}_4 \rightarrow 2 \text{ Cl}_2 + 3 \text{ O}_2 + 8 \text{ H}_2\text{O} + 2 \text{ N}_2\text{O}$$

represents the majority of the products. At higher temperatures more nitric oxide (NO) is produced. Between 350 °C and 450 °C gas analysis of the products of thermal decomposition gives

$$10 \text{ NH}_4\text{ClO}_4 \rightarrow 2.5 \text{ Cl}_2 + 6.4 \text{ O}_2 + 18.8 \text{ H}_2\text{O} + 2 \text{ N}_2\text{O} + 2.5 \text{ NOCl} + \text{HClO}_4 + 1.5 \text{ HCl} + 1.75 \text{ N}_2.$$

Thus the decomposition of AP in supercritical water avoids the formation of the hazardous products (Cl₂, NOCl) formed in thermal decomposition.

Above 450 °C, ammonium perchlorate detonates. The possibility of explosive energy release was investigated. Concentrated solutions of ammonium perchlorate (1.0 M, 122 g/L) were rapidly heated to temperatures over 600 °C at pressures near 340 atm in a small batch reactor. Neither pressure nor temperature transients indicative of rapid energy release was observed. These results indicate SCWO is, therefore, more controlled, i.e., safer than thermal decomposition.

Reactor Corrosion. Corrosion of metals and alloys at high temperature and pressure is an important issue for applying supercritical fluid technology to the treatment of hazardous wastes. Corrosion may in fact be a cost-limiting factor for the scale-up to large SCWO facilities. Corrosion is inherently electrochemical in nature. An understanding of the oxidation-reduction reaction chemistry in supercritical environments is essential for eventual control of these corrosion processes. The most corrosive substance we have run to date is ammonium perchlorate. When running AP in the C-276 alloy reactor corrosion was a problem as we first noted by the dark-colored effluent. Analyses are presented in Table VI. Most corrosion products formed insoluble salts in supercritical water. While it was generally possible to flush the insoluble salts out of the reactor during the cool-down phase, the reactor eventually plugged and could not be reopened. The gold-lined reactor was built to avoid these corrosion problems.

TABLE VI. Corrosion Products for SCWO of Ammonium Perchlorate

Reactor	Au (ppm)	Cr (ppm)	Fe (ppm)	Mo (ppm)	Ni (ppm)
C-276 reactor		130.00		54.00	39.00
Gold lined Stainless reactor (acidic)	1622.00	3.36	65.38		55.04
Gold lined Stainless reactor (alkaline)	0	0.99	0.99		3.73

We have run AP in the gold-lined reactor in both alkaline and acidic solutions. Significant corrosion is observed in acidic solutions of AP. At low pH, the oxidation of gold, $Au^0 \rightarrow Au^{+3} + 3e^-$ is activated. The oxidant could be NO_3^- produced in the decomposition of AP or the perchlorate itself. The gold complexes with chloride ion and is dissolved into solution as $AuCl_4^-$. These reactions are analogous to the well known dissolution of gold in aqua regia. By raising the pH, this corrosion pathway is blocked as shown in Table VI. What little corrosion we do see probably occurred on exposed, hot stainless portions of the reactor. In contrast with AP, other explosives have exhibited very little corrosivity.

CONCLUSIONS

In general, the chemistry of oxidation of energetic materials in supercritical water is very similar to that found previously for other classes of organics. We have established conditions for which the hydrocarbon elements of all the energetic compounds investigated thus far are completely oxidized to CO2 and H2O. The temperature, residence time and oxidant concentration necessary to achieve complete oxidation vary, depending on the nature of the energetic material. Our results indicate that complete oxidation is always achievable using excess oxidant and operating the linear reactor at 600 °C (11 s residence time). Reasonable carbon balances are obtained for all the energetic materials investigated under these conditions, including PETN, HMX, TNT, RDX, and NQ. Most of the carbon is detected as CO2, with some small fraction remaining in solution as inorganic carbon (CO₃²- or HCO₃⁻). The exception is NQ, which produces large quantities of inorganic carbon. The conditions that produce these results were deliberately "extreme" to ensure complete oxidation. We have not adequately explored the dependence of the chemistry on oxidant concentration and temperature to determine optimum conditions. Minimization of oxidant concentration is important since the oxidant represents a large fraction of the process cost and if present in excess may enhance corrosion or cause the formation of undesirable products. Furthermore, we have very little data for one variable, the reactor residence time. Less "extreme" conditions (e.g., lower temperatures and 1:1 oxidant stoichiometries) may be sufficient to achieve complete oxidation given longer residence times. Without added oxidant, products of incomplete oxidation were often observed, including CO, CH4 and HCN.

The nitrogen chemistry of energetics is considerably more complicated, varying widely depending on the nature of the starting material. The nitrogen is always distributed among a group of products, N₂, N₂O, NO₂- and NO₃-, having formal oxidation states of N varying from 3- to 6+. Quantitative data have been obtained for all products except N₂. The latter is implicated as the major N product in many of the reactions by elimination of other possible products. Qualitative data (Mass Spectroscopy and Gas Chromatography) indicate N₂ production in the case of NM, NQ and TNT. No obvious correlation exists between the nitrogen content or the type of nitrogen groups (e.g., NO₂ or NH₂ groups) of a particular energetic material and the distribution of nitrogen products (N₂, N₂O, NO₂- and NO₃-). It is possible, however, to vary the distribution of products in the different oxidation states by varying the temperature and the oxidant concentration.

The clearest example of this tunability is NO_x^- production in the reactions of TNT. When a large excess of oxidant is employed at 600 °C, a significant fraction of the initial N (74%) is converted to NO_x^- . This fraction is much less (12%) for a small (5-fold) excess of oxidant and yet complete oxidation of the carbon still occurs. The same trend is observed for the oxidation of RDX with excess H_2O_2 (10% NO_3^-) and with oxygen balance (no NO_3^-). These results indicate that significant control over the oxidation chemistry is possible through the precise tuning of reaction parameters.

The destruction chemistry of AP in SCWO is unique among the energetic materials since AP has no carbon, and is a strong oxidant. The chemistry is best described by the following equation:

$$NH_4ClO_4 + NaOH \rightarrow NaCl + 2.5 H_2O + 0.4 N_2 + 0.1 N_2O + 1.2 O_2.$$

Conditions have been determined for which 99.6% of the ClO₄⁻ is destroyed. The Cl is converted to Cl-, formally reduced from 7+ to 1-, and excess oxygen is produced in the reaction. Further evidence for the highly oxidizing nature of this reaction is provided by the strong oxidative corrosion of the C-276 and 316 stainless reactors. The addition of reducing equivalents, in the form of a fuel such as a hydrocarbon, may improve the destruction of AP as well as reduce the reactor corrosion. The nitrogen is distributed between N₂ and N₂O, with no formation of higher oxides or NOx⁻. In contrast to thermal decomposition of solid AP, no harmful products such as Cl₂ or NOCl are formed in the SCWO reactions.

A critical issue for practical application of an SCWO process to the treatment of energetic materials is reactor wear caused by corrosion. Corrosion of the C-276 reactor by most of the energetic materials does not appear to be a problem. The exception is AP, which caused severe corrosion of the C-276 and 316 stainless reactors. For laboratory scale reactors, this problem has been solved by the use of a gold liner in the SCW region, which reduces corrosion to acceptable levels.

ACKNOWLEDGMENTS

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Removal of Volatile Organic Compounds (VOC's), Acetone and Ethyl Alcohol Emitted in the Manufacture of a Multi-Base Propellant

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Introduction

In the manufacture of multi-base propellants, volatile organic compounds (VOC's) are emitted from the manufacturing process. Currently, air pollution requirements by states and the U.S. Environmental Protection Agency (EPA) necessitate a reduction in VOC emissions. Jake (1987) reported that an acceptable emission level is achieved if the feed organic content at the gas discharge is reduced by eighty-five percent, as was achieved at the Radford Army Ammunition Plant (RAAP) in Radford, Virginia during laboratory studies. This has not been implemented because of the presence of nitroglycerin (NG) in the vapor.

The Production Base Modernization Activity located at Picatinny Arsenal, a member organization of the Hazardous Substance Management Research Center (HSMRC) at New Jersey Institute of Technology, has requested that the HSMRC study the removal of the VOC's, acetone and ethyl alcohol, from the emissions originating in multi-base propellant production by absorption in concentrated sulfuric acid. [Private Communication, 1991]

The two principal areas of VOC pollution in the manufacture of the multi-base propellants are in the mixer unit and in the forced air dry (FAD) unit.

a. Mixer unit:

In the propellant blending unit, the VOC concentrations are estimated to be 450 ppm by volume acetone, 900 ppm ethyl alcohol, and 2-14 ppm nitroglycerin (NG), for a flow rate of about 1,000 cubic feet per minute (CFM). The bulk of the emissions are generated approximately twice a shift during a fifteen minute 'blow-down' cycle when an inert gas is passed through the mixer unit.

b. Forced air dry (FAD) unit:

The FAD unit is a batch drying unit operation. The approximate maximum concentrations of VOC's encountered in this operation are 1,200 ppm by volume acetone, 1,850 ppm ethyl alcohol and 2-14 ppm NG. The flow rate in about 1,500 CFM per bay (a basic propellant drying area) with four bays constituting a FAD. The VOC concentrations at the end of the 38 hour drying cycle are essentially zero. The operating temperature varies from ambient to a maximum of 140 °F (60 °C). Approximately 50% of the emissions are lost during the loading of the bay (this includes those emissions generated during transporting the propellant from the cutting area to the FAD area). [Langford, T. H. et. al., 1983]

Process propellant quantity limitations permit operating two bays simultaneously. The two remaining bays in a FAD unit are on turn-around. Hence, a gas absorption unit should have as a design basis the removal of the VOC emissions from two operating bays.



Absorption of solvents with sulfuric acid is one of the oldest methods of solvent recovery. It was first used for the recovery of alcohol and ether in the manufacture of artificial silk by the old Chardonnet process and was then widely applied in the manufacture of powder in Germany and Austria before and during World War I. The air containing alcohol and ether entered the tanks filled with sulfuric acid. The tanks were cooled from the outside by spraying with water.

At the Troisdorf powder factory near Cologne, lead towers were sprayed on the inside with sulfuric acid which was used for the absorption of the solvent. Air containing alcohol and ether entered from below in countercurrent flow relative to the sulfuric acid. The solvents were distilled from the sulfuric acid by heating to 120 °C. Alcohol was then partly converted into ether. The yield was low; only 10-12 percent of solvent used for the manufacture of the powder was recovered. The disadvantages of this method were numerous and the method is no longer in use. [Urbanski, 1967]

The U.S. Army has demonstrated the removal of acetone and ethyl alcohol from a vapor stream on a laboratory scale using concentrated sulfuric acid. [Jake, 1987] U.S. Army multi-base propellant and munitions manufacturing plants have sulfuric acid concentration facilities capable of producing 90 percent acid from 70 percent acid by vacuum evaporation. In addition, there are oleum producing facilities capable of producing 109 percent sulfuric acid from 70 percent spent acid by burning sulfur to form sulfur dioxide (SO₂), converting the SO₂ to sulfur trioxide (SO₃), followed by absorption of the SO₃ in sulfuric acid to form oleum. Because of availability, sulfuric acid would be a desirable absorbing agent into which the VOC's can be absorbed to reduce plant emissions. Other studies have been cited extensively by Jake (1987).

Literature

There is a paucity of published data for the removal of acetone and ethyl alcohol using sulfuric acid. Ormandy (1929) has studied the removal of acetone vapors from air using concentrated sulfuric acid and phosphoric acid. Other absorption agents that were used are: water, cresols, and sodium bisulfite solutions. The use of sodium bisulfite would involve absorption with chemical reaction. Generally, the concentrations of acetone used were much higher than needed for this proposal study, and ranged up to about 26,000 ppm in air. Ormandy described two laboratory experimental methods, including a description of both apparatus and analytical techniques. A flow diagram of a proposed plant was also presented by Ormandy (1929).

Robinson (1942) presented data on the recovery of diethyl ether in sulfuric acid. Vaporliquid equilibrium data were given at various concentrations of sulfuric acid at 20 °C. [Robinson, 1942] No vapor-liquid equilibrium data could be located for ethyl alcohol nor nitroglycerin (NG) using concentrated sulfuric acid as the solvent.

Jake (1987) reported on using concentrated sulfuric acid as a solvent and expanded on Oramandy's study (1929). Using a laboratory absorption bottle Jake measured break-through times as a function of the percent inlet gas solute that is removed. The concentrations of sulfuric acid ranged from 76 percent to 95 percent and solution temperature ranged from 6 °C to 37 °C. Jake concluded that concentrated sulfuric acid as solvent is superior to sodium bisulfite from the view of capital costs, and that cold sulfuric acid is an excellent absorbent.

This Study

The objectives of this study are:

- o To measure vapor-liquid equilibrium data for the systems :
 - acetone sulfuric acid
 - ethyl alcohol sulfuric acid
 - ethyl ether sulfuric acid

at concentrations of 76 percent and 96 percent and at temperature ranging from 15 °C to 54 °C.

- To study the absorption of the VOC's, acetone and ethyl alcohol in a packed gas absorption column with recirculating sulfuric acid.
- To develop a complete, computerized material and energy balance on a prototype plant to remove VOC's from the mixer unit and FAD unit.

Vapor-liquid Equilibrium Study

A search of the literature indicates that acetone, ethyl alcohol and diethyl ether will react with sulfuric acid. Jake (1987) indicated that nitroglycerin is destroyed by concentrated sulfuric acid by the formation of nitric oxide (NO_X) compounds which in turn are absorbed by the sulfuric acid. Some of the reactions found are shown in Tables 1 - 3. These reactions were found in standard organic chemistry textbooks. Table 1 shows the reactions of acetone and sulfuric acid. Table 2 shows the reactions of ethyl alcohol and sulfuric acid. [Feiser, L. F. & Feiser, M., 1957] Table 3 shows the reactions of diethyl ether and sulfuric acid. [Robinson, 1942]

Table 1. Reactions between Acetone and Sulfuric Acid

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ C = C \\ CH_{3} \\ C = C \\ C \\ C \\ CH_{3} \\ C = C \\ C \\ C \\ CH_{3} \\ CH_{3} \\ C \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ C \\ CH_{3} \\ CH_{$$

Mesityl oxide: colorless, bp. 131 °C

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} = \begin{array}{c} \text{C} \\ \text{C} \end{array} + \begin{array}{c} \text{C} \\ \text{C} \end{array} = \begin{array}{c} \text{C} \\ \text{C} \end{array} + \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{C} \\ \text{C} \\ \text{C} \\ \text{C} \end{array} + \begin{array}{c} \text{C} \\ \text{C} \end{array} + \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} + \begin{array}{c} \text{CH}_{2} \\ \text{C} \\ \text{C}$$

yellow crytalline solid, mp. 28 °C, bp. 197.2 °C

Other condensation product produced:

$$\begin{array}{c} \text{CH}_{3} \\ \text{H} \\ \text{C} \\ \text{H} \\ \text{C} \\ \text{C} \\ \text{H} \\ \text{C} \\ \text{C} \\ \text{C} \\ \text{H} \\ \text{C} \\ \text{C}$$

low yield, colorless, mp. -44.8 °C, bp. 164.8 °C

Table 2. Reactions between Ethyl Alcohol and Sulfuric Acid

$$CH_{3}-CH_{2}-OH + HO-SO_{2}-OH \xrightarrow{conc.} H_{2}SO_{4}$$

$$CH_{\overline{3}}-CH_{\overline{2}}-O-SO_{\overline{2}}-OH + H_{2}O$$

$$Ethyl Sulfuric Acid$$

$$Ethyl Hydrogen Sulfate$$

$$(2.a)$$

Proceeds to completion with excess H₂SO₄ at 0 °C. H₂O reverses reaction

Diethyl Ether; colorless liquid, bp. 34.6 °C

Both ethylene and diethyl ether which are byproducts at 170 °C and 140 °C have small diferences in optimum temperature.

Table 3. Reactions between Diethyl Ether and Sulfuric Acid

$$CH_3 - CH_2 - O - CH_2 - CH_3 + H_2SO_4 \xrightarrow{20 \text{ °C}}$$

$$CH_3 - CH_2 - O - SO_2 - OH + HO - CH_2 - CH_3$$

$$Ethyl Sulfuric Acid Ethyl Alcohol$$
(3.a)

Ethyl alcohol reacts with Sulfuric Acid:

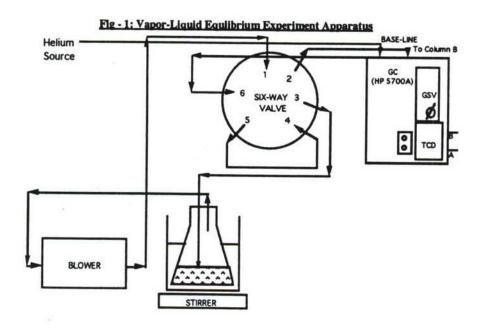
$$CH_{3}-CH_{2}-OH + H_{2}SO_{4} \xrightarrow{20 \text{ °C}}$$

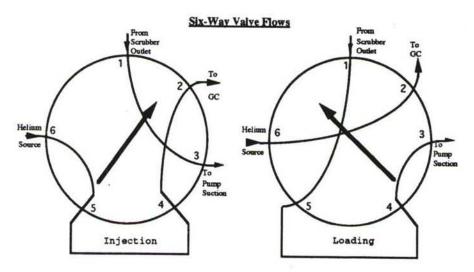
$$CH_{\overline{3}}-CH_{\overline{2}}-O-SO_{\overline{2}}-OH + H_{2}O$$

$$Ethyl Sulfuric Acid Water$$
(3.b)

Experimental Apparatus

The experimental apparatus is shown in Figure 1. A Hewlett Packard, 5700 A Gas Chromatograph was used with a ten foot stainless steel column, 1/8 inch in diameter, packed with Supelco, Catalog Number, 1 - 1813 M, 80 / 120 Carbopack B / 3%, SP - 1500 packing. The flask used for the calibration curve study had a volume of 4360 ml which was carefully measured. Known amounts of liquid organics were added with a 10 micro-liter syringe. The recirculating blower was a Teflon Diaphragm Vacuum Pump (Cole Palmer, Catalog No. L - 07056 - 22). It has a single pump head configuration, a maximum vacuum of 25 inches of mercury, a maximum discharge pressure of 25 psi and flow rate of 0.57 cubic feet per minute. For equilibrium studies, the 4360 ml flask was replaced with a 500 ml flask. This experimental method is a modified version of that used by Ormandy (1929). The sample loop in the Six-Way Valve was 3.0 ml.





Experimental Procedure

Calibration

Known amount of liquid organics were added to the 4360 ml flask shown in Figure 1 that had been flushed with nitrogen. The conditions used for calibration are shown in Table 4. The purity of the reagents is shown in Table 5.

Table 4. HP5700A GC Operating Conditions

Carrier Gas:

Helium at a rate of 20 ml / min

Oven Temperature:

80 - 110 °C sequencing at a rate of 4 °C / min

150 °C

6.95

Detector Setting:

Sensitivity - 6 Attenuation - 4

liter

Temperature -

Sample Circulation Rate:

0.13 cubic feet / min

Retention Time; minutes

Air 1.27 Ethyl Alcohol 3.12 Acetone 4.25

Ethyl Ether

Table 5. Reagents Used in This Study

or 3.68

Sulfuric Acid. H

 H_2SO_4

Fisher Scientific Co.,

A 300^c - 212 Reagent Grade ACS

Min. 95 % by weight Max. 98 % by weight

Specific Gravity 1.84 Normality 36 Ethyl Alcohol. CH3CH2OH

/ min

Fisher Scientific Co.,

A 962 - 4 Reagent Alcohol

Anhydrous Alcohol, Vol. 90 % ± 1 %

Denaturants Added, volume

Methyl Alcohol, 5 % Isopropyl Alcohol 5 %

Acetone. CH₃CO CH₃

Fisher Scientific Co., A 18 - 4 Certified ACS

Density 0.7854 gm/ml at 25 °C

Boiling Point 56.1 °C ± 0.1 °C

Denaturants Added, volume

Isopropyl Alcohol 0.01 % Methanol 0.02 % Water 0.3 %

Diethyl Ether. CH3CH2OCH2 CH3

Mallinckrodt UN 1155 Anhydrous Analytical Reagent

Density 0.7077 gm/ml at 25 °C

Water 0.005 %



Equilibrium Studies

Known amounts of liquid organics were added to 100 ml of sulfuric acid. The concentrations of sulfuric acid which were used were 76 percent by weight and 96 percent. Initial tests were made at room temperature. However, a large quantity of heat of mixing was observed and, hence, the acid and the organic were then both cooled to 0 °C before mixing. The system was blanketed with nitrogen and the gas phase was recirculated. The temperature of the sulfuric acid solution was controlled at the desired temperature between 15 °C and 54 °C. After equilibrium was established, three different samples were trapped in the sample loop of the sixway valve (Figure 1) and then swept into the GC column directly. The average of these three analyses was used for the correlations. Operating conditions for the Gas Chromatograph are shown in Table 4.

Experimental Results

Calibration

The calibration curve is shown in Figure 2 for acetone, ethyl alcohol and diethyl ether.

Equilibrium Studies

Prior to making the equilibrium studies, the method and apparatus used were verified by comparison with previous studies. Figure 3 shows a comparison of the measurements of acetone with the data of Ormandy (1929). Agreement is excellent. Figures 4 and 5 show the data for diethyl ether compared with the data of Robinson (1942). Agreement is also excellent. With the experimental technique established, vapor-liquid equilibrium data were developed for acetone, ethyl alcohol, and diethyl ether in 76 percent by weight sulfuric acid and 96 percent by weight acid. Figure 6 shows the data for acetone in 76 percent by weight sulfuric acid as a function of temperature. The mole fraction of acetone in the air is far in excess of the concentration that will result in this study (1,200 ppm in the feed gas). Figure 7 shows the data for ethanol in 76 percent acid. As expected, for a given mole fraction of acetone, or ethanol in the liquid phase, the mole fraction in the vapor phase rises with the temperature. Figures 8 and 9 show the equilibrium data for acetone and ethyl alcohol in 96 percent by weight sulfuric acid. There is no trace of acetone or ethyl alcohol in the vapor phase.

Fig - 2: HP 5700A GC - Calibration Curve [Acetone, Ethanol, and Ethyl Ether In Air]

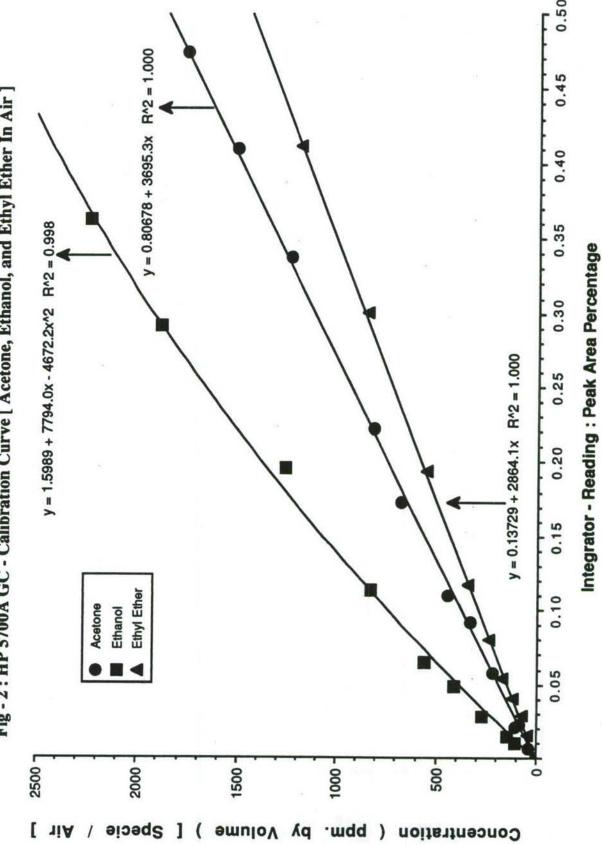




Fig-3: Acetone in Air equilibrium with mixtures of Acetone and diluted Sulfuric Acid [Compared with Ormandy's]

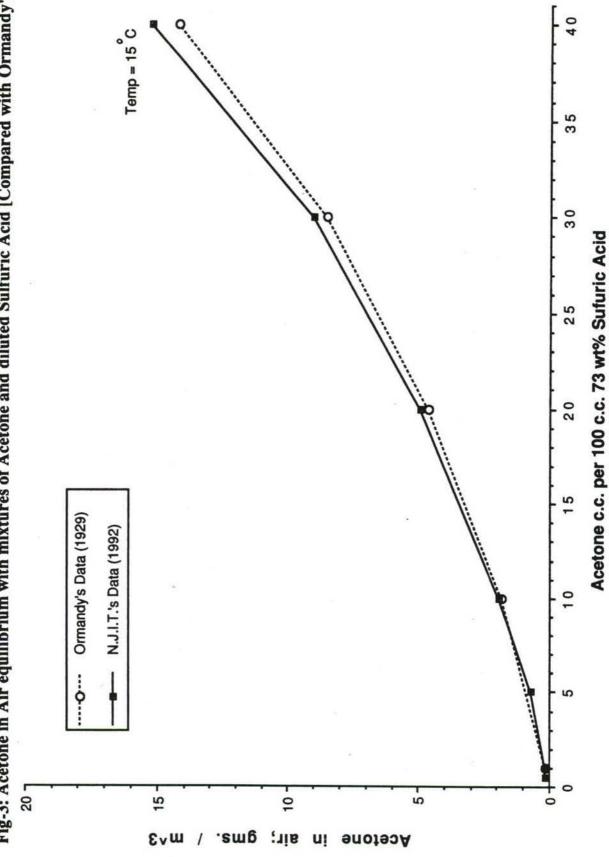


Fig-4: Ethyl Ether in Air equilibrium with mixtures of Ethyl Ether and 96 wt% H2SO4 [Temp = 20°C] 0.20 0.15 Robinson's Data (1942) 0.10 N.J.I.T.'s Data (1992) 0.05 0.00 0.0030 J 0.000.0 0.0025 0.0020 0.0010 0.0015 0.0005 fraction; ether alom



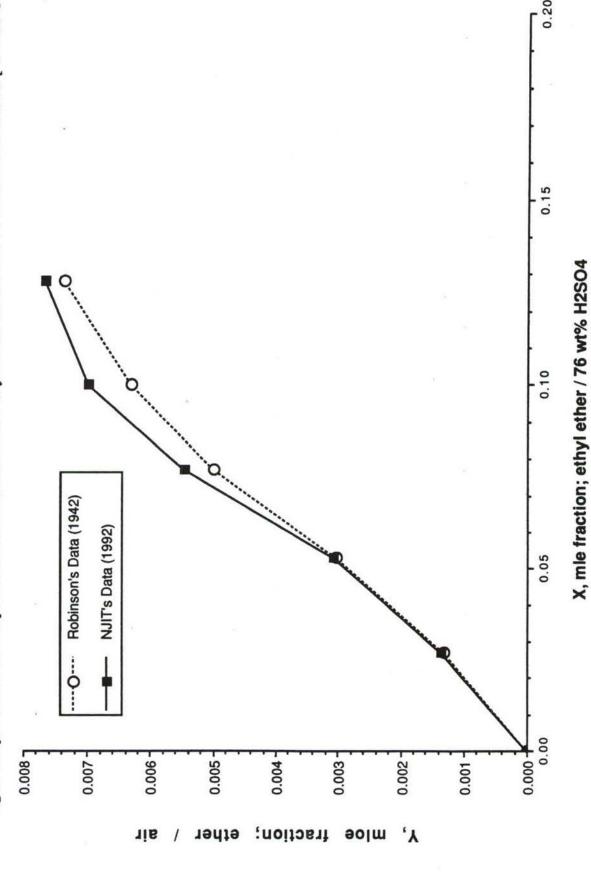


Fig - 6: Acetone In Air equilibrium with mixtures of Acetone and diluted Sulfuric acid at Various Temperatures 0.20 X, mole fraction; Acetone / 76 wt % Sulfuric Acid 0.15 0.10 23 C 24 C 54 C 0.03 7 0.02 0.01 Y, mole fraction; acetone

Fig - 7: Ethanol In Air equilibrium with mixtures of Ethanol and dilute Sulfuric Acid at Various Temperatures

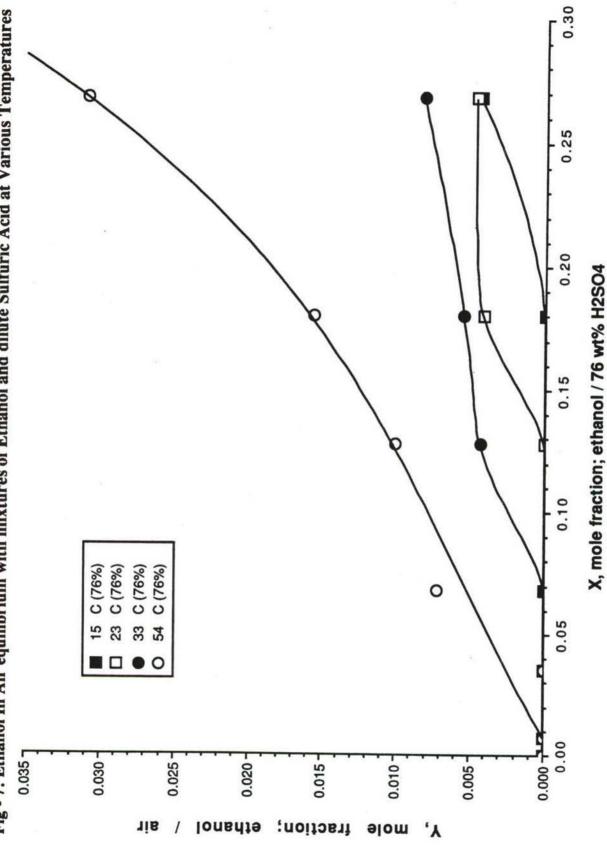


Fig-8: Acetone in Air equilibrium with mixtures of Acetone and concentrated Sulfuric Acid (Mix with cooling) 0.25 0.20 0.15 C; 96 wt% C; 96 wt% 33 C; 96 wt% 23 C; 96 wt% 24 15 0 0.05 0.00000.0 0.00 0.00040 0.00010 0.00035 0.00015 0.00030 0.00025 0.00020 0.00005 acetone fraction; mole

X, mole fraction; acetone / 96 % H2SO4

Fig-9: Ethanol in Air equilibrium with mixtures of Ethanol and concentrated Sulfuric Acid (Mix with cooling)

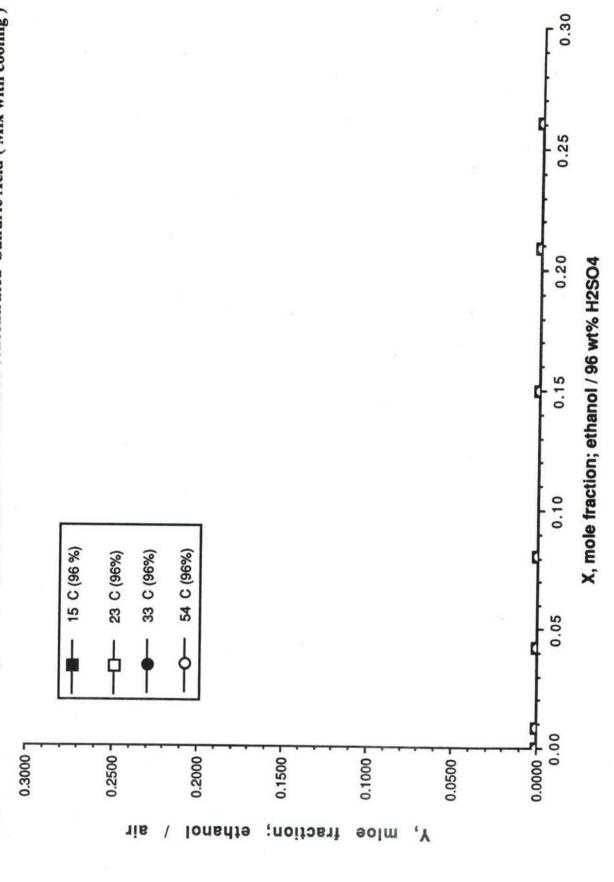
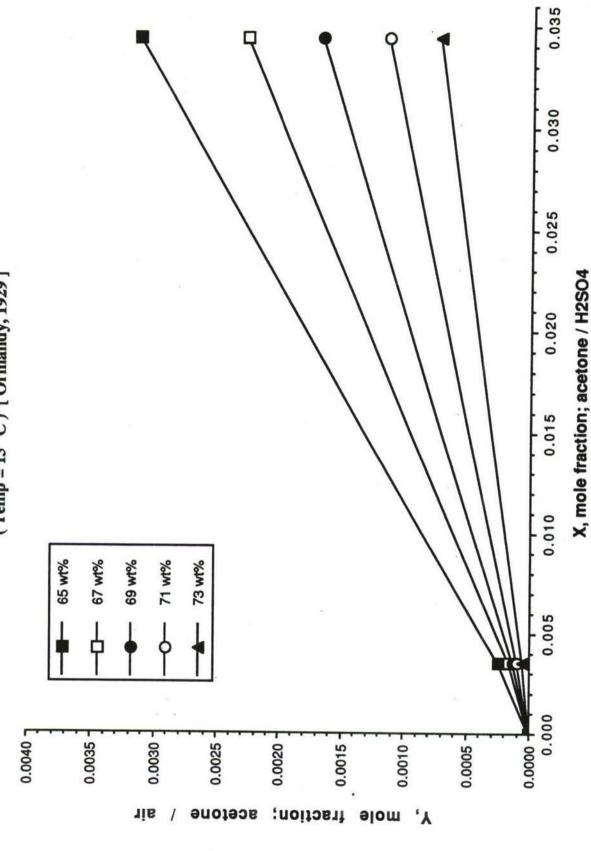


Fig-10 : Acetone in air equilibrium with mixtures of acetone and Various Concentrations of Sulfuric Acid (Temp = 15 $^\circ$ C) [Ormandy, 1929] 0.035 0.025 X, mole fraction; acetone / H2SO4 0.020 0.015 0.010 65 wt% 67 wt% %JM 69 71 wt% 73 wt% 0 wt% 0.000 0.0407 A 000.0 0.035 0.030 0.025 0.020 0.015 0.010 0.005 fraction; acetone mole

Fig-11: Acetone in air equilibrium with mixtures of Acetone and Various Concentrations of Sulfuric acid (Temp = 15 $^{\circ}$ C) [Ormandy, 1929]



80 Fig-12: Acetone-Sulfuric Acid System; Equilibrium constant vs. Weight Percent Sulfuric Acid (Temp = 15 C) [Ormandy, 1929] 65 y = 1.1479 - 0.022398 x + 0.000094657 x² 60 55 20 H2SO4 (Wt %) 40 35 30 20 15 10 1.27 0.9 0.8 -1.0-0.7 0.6 0.5 0.4 0.0 Ξ 0.3 0.2 0.1 Constant Equilibrium



Fig-13: Ether in air equilibrium with mixtures of Ether and Weight Percent Sulfuric Acid (Temp = $20~\rm C$) [Robinson, 1942]

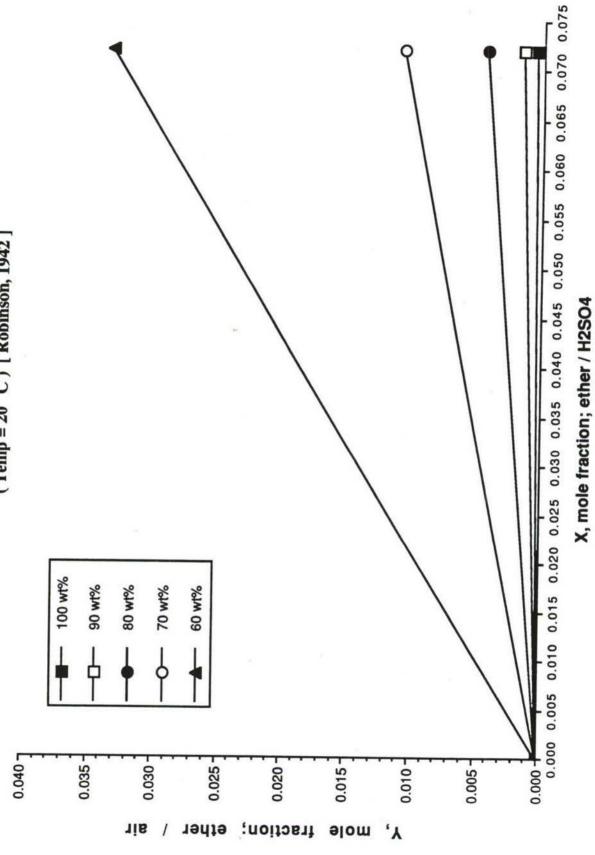


Fig-14: Ether - Sulfuric Acid System: Equilibrium Constant vs. Weight Percent Sulfuric Acid (Temp = 20 C) [Robinson,1942] $y = 194.54 * 10^{4} (-0.043951 \times)$ H2SO4 (wt %) 09 0.57 0.0 0.4 0.3 0.1 0.2 Constant Equilibrium



Discussion of Results

Vapor-Liquid Equilibrium Data presented by Ormandy (1929) in the dilute region are shown in Figures 10 and 11. The slope of the graph in the dilute region is a measure of Henry's Law constant. Figure 10 also shows the data for acetone in water (0 % sulfuric acid). Figure 11 shows that as the concentration of acid rises, the slope decreases. Figure 12 shows a correlation of equilibrium constant and sulfuric acid concentration. The graph shows that the equilibrium constant approaches zero in the vicinity of 75 percent sulfuric acid by weight for low concentrations of acetone in the liquid. This fact is verified in Figure 6 for 76 percent by weight sulfuric acid and in Figure 8 for all concentrations of acetone in 96 percent by weight sulfuric acid. Hence, using 96 percent acid removes all acetone from the vapor phase.

The same analysis was used with the Robinson (1942) data for diethyl ether. Figure 13 shows that in the dilute region, the equilibrium constant falls as the concentration of sulfuric acid rises. Figure 14 shows that the equilibrium constant approaches zero in the vicinity of 96 percent sulfuric acid but does not drop to zero. This fact is shown in Figure 4.

There are no available published data for ethyl alcohol in sulfuric acid. Figure 7 shows that at low concentrations and low temperatures, the concentration of ethyl alcohol in the vapor is nil with 76 percent sulfuric acid. In Figure 9, the data for 96 percent sulfuric acid show no trace of ethyl alcohol at all concentrations and all temperatures.

Unknowns Observed During Vapor-Liquid Equilibrium Studies:

In the studies using 76 percent sulfuric acid no unknowns appeared during the acetone and diethyl ether runs. With ethyl alcohol, at high concentrations and at temperatures above 34 $^{\circ}$ C, the methyl alcohol (CH₃OH) impurity in the reagent grade ethyl alcohol (C₂H₅OH) appeared at a retention time of 2.05 minutes and the isopropyl alcohol impurity appeared at 4.96 minutes.

With acetone in 96 percent sulfuric acid, sulfur dioxide (SO₂) was detected at the retention time of 1.92 minutes above 34 $^{\circ}$ C. These analyses were made using a HP 5988 Mass Spectrograph coupled with a HP 5890 Gas Chromatograph. The column for this system was a 50 meters long and 0.32 mm in diameter cross-linked methyl-silicone capillary column. The carrier gas (Helium) rate was 1mL/min. Temperature sequencing was, initial temperature 30 $^{\circ}$ C (hold 2 minutes) then increase temperature at 4 $^{\circ}$ C/min to final temperature 160 $^{\circ}$ C (hold 5 minutes). 2-methyl-propanol or butenol (C₄H₈O) was detected at a retention time of 12.3 minutes using the HP 5890 only. With ethyl alcohol in 96 percent sulfuric acid, sulfur dioxide (SO₂) was detected at a retention time of 1.92 minutes. Above 54 $^{\circ}$ C, C₄H₈O was detected along with CH₃OH and isopropyl alcohol using the HP 5890 only. With diethyl ether and 96 percent sulfuric acid, C₆H₁₄O₂ (Retention Time = 13.2 minutes) and C₄H₈O (Retention Time = 12.6 minutes) were detected using the HP 5890 only.

If temperatures reach higher levels, the acetone, ethyl alcohol and diethyl ether with 96 percent sulfuric acid may yield other compounds. Sulfur dioxide (SO₂) will also be stripped out of the acid by the gas flow.



Gas Absorption Studies

Concentrated Sulfuric Acid can be used as an absorbent of acetone and ethyl alcohol from air in a countercurrent packed gas absorption column.

In a packed gas absorption system, the packed height can be calculated from the equation 1.

$$Z=N_{GG}H_{GG}$$
 (1)

The number of transfer units is calculated from the equation 2.

$$N_{CG} = \int_{y_1}^{y_2} \frac{dy}{y - y}$$
 (2)

In the dilute region, the operating line for the column, with a slope, L/G, is a straight line and the equilibrium line with a slope, m, is also a straight line. Hence, the equation 2 reduces to equation 3.

$$N_{CG} = \frac{y_1 - y_2}{\left| y_1 - y_1^* \right| - \left| y_2 - y_2^* \right|} \\ \left| n \frac{y_1 - y_1^*}{\left| y_2 - y_2^* \right|} \right|$$
(3)

The height of the transfer unit HOG is related to the mass transfer coefficient by equation 4.

$$H_{OG} = \frac{G}{K_{va}}$$

at the overall resistance is the sum of two film resistances

The two film theory shows that the overall resistance is the sum of two film resistances from equation 5.

$$\frac{1}{K_{y}a} = \frac{1}{k_{y}a} + \frac{m}{k_{x}a} \tag{5}$$

Thus, it can be shown (Foust etal, 1980) from equation 5.

$$H_{OG} = H_G + H_L \frac{mG}{L}$$
(6)

Literature

Othmer and Scheibel (1941) studied the absorption of acetone with water in a packed gas absorption column and presented an equation for the overall mass transfer coefficient. Scheibel and Othmer (1944) studied the absorption of various ketones with water.

Leva (1953) reported the Scheibel - Othmer studies and referred to the work of Larson (1942) for the absorption of acetone with water. Sherwood and Holloway (1940) reported that in the absorption of ammonia, when sulfuric acid was used instead of water, absorption coefficients were 50 -70 percent greater. When water was used alone, the liquid film resistance was an appreciable fraction of the total resistance. Thus, addition of the acid reduced the liquid film resistance.

Tamir (1986) studied the absorption of acetone from air into water using a two-impinging stream absorber. Molstad and Parsly (1950) studied the absorption of ethyl alcohol vapors from air with water in packed towers.

This Study

Calculations for 1 - inch ceramic Raschig rings indicate that the mixer unit would require a column diameter of 2.5 feet and the FAD unit would require a column diameter of 4.5 feet. The results of calculations are summarized in Table 6 for 85 percent removal of the VOC's.

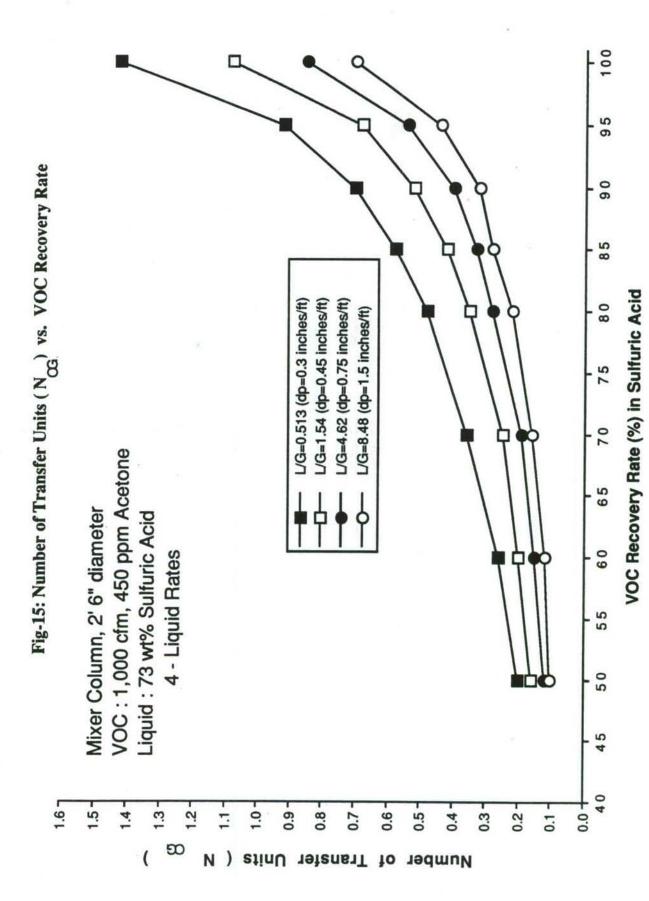
Table 6. Height of Column (85 % removal, 1 inch Ceramic Raschig Rings)

$$Z = N_{OG} * H_{OG}$$

		<u>M</u>	ixer Unit	FAD Unit		
		H ₂ O	$H_2SO_4(73\%)$	H_2O	$H_2SO_4(73\%)$	
L=	moles / hr	407	211	1220	211	
G =	moles / hr	137	137	411	411	
	CFM	1000	1000	3000	3000	
	ppm Acetone	450	450	1200	1200	
L/G	(Mass Ratio)	1.8	2.8	1.8	0.79	
	are Drop, of water ft of packing	0.8	0.45	0.6	0.25	
Colun	nn Diameter, ft	2.5	2.5	4.5	4.5	
Nog		1.6	0.44	1.6	0.58	
H_{OG}	(estimated), ft	3.5	7.4	3.5	7.4	
Z,	ft	5.6	3.3	5.6	4.3	

Curves were also presented for N_{OG} as a function of percent VOC removal at various L/G ratios and acid strengths for both the mixer unit and FAD unit. For 73 percent acid the curves are shown in Figure 15 and 16. The results are summarized in Table 7 for 85 percent removal of the VOC's.





100 95 Fig - 16 : Number of Transfer Units (N) vs. VOC Recovery Rate $_{\text{CG}}$ 06 85 80 L/G=0.513 (dp=0.25 inches/ft) L/G=1.54 (dp=0.45 inches/ft) L/G=4.62 (dp=0.50 inches/ft) L/G=10.3 (dp=1.5 inches/ft) 75 Forced Air Drier Column (FAD), 4' 6" diameter 20 VOC: 3,000 cfm, 1,200 ppm Acetone 65 Liquid: 73 wt% Sulfuric Acid 09 4 - Liquid Rates 55 50 45 1.6 .5. 4. .3 -2 0.0 1.0 6.0 -8.0 0.7 9.0 0.5 0.4 -0.3 0.1 0.2 œ of Transfer

Number

VOC Recovery Rate (%) in Sulfuric Acid



Table 7. Effect of Acid concentration on NOG

Mixer - 2	ft and	6 inches	in Diameter
TATEL A	A T P POTTER	OHIGHES	III PIMILICUL

% H ₂ SO ₄	N _{OG}	L/G (molar)	Pressure Drop inches of water / ft of packing
73	0.44	1.54	0.45
65	0.64	1.73	0.50
0	1.60	2.97	0.80
AD - 4 ft and 6 inches	in Diameter		
% H ₂ SO ₄	Nog	L/G (molar)	Pressure Drop
-			inches of water / ft of packing
73	0.58	0.51	0.25
65	0.64	1.73	0.45
0	1.60	2.97	0.60

The effect of rising acid strength is to markedly reduce the N_{OG} needed and, hence, this results in a shorter packed height. Since the slope of the equilibrium line becomes zero for 76 percent and 96 percent acid, the N_{OG} values approach $ln (y_1/y_2)$ [Equation 3]. Hence, with these acid strengths almost any type of contacting system can remove the VOC's from air.

An estimate of the H_{OG} needed can be made using the data given by Othmer and Scheibel (1941). At operating conditions in the FAD unit, calculations indicate that about 74 percent of the resistance would be in the gas phase when using water. The constants in Equation 6 were determined from the Othmer's and Scheibel's data. The data are shown in Figure 17 for the acetone-air-water system. Hence, Equation 6 can be estimated to be Equation 7 for this system.

$$H_{OG} = 2.3806 + 2.9482 \frac{mG}{L} \tag{7}$$

For the acetone-air system, the gas film resistance should not change with the change in solvent. Sherwood and Holloway (1940) showed that the H_{L_1} in Equation 6, which would change with solvent, can be estimated from Equation 8.

$$H_{L} = \frac{1}{a} \left(\frac{L}{\mu} \right)^{n} \left(\frac{\mu}{\rho D} \right)^{s} \tag{8}$$

Hence, using H_L for acetone-water of 2.95 from Equation 7, H_L for acetone- H_2SO_4 can be estimated by Equation 9.

$$\frac{\left(H_{L}\right)_{\text{acetone}-H_{2}SO_{4}}}{\left[H_{L}\right]_{\text{acetone}-H_{2}O}} = \frac{\mu_{H_{2}O}}{\mu_{H_{2}SO_{4}}} \left[\frac{N_{\text{sc}_{\text{acetone}-H_{2}SO_{4}}}}{N_{\text{sc}_{\text{acetone}-H_{2}O}}}\right]^{\text{s}} \tag{9}$$



9.0 L = 455 - 685 lb/ft^2-hr Fig-17: Height of Transfer Unit vs. mG / L; System: Acetone-Air-Water 0.5 0.4 mG/L 0.3 y = 2.3806 + 2.9482x R² = 0.816 0.2 0.1 0.0 57 4 9-2 90 . IJ Н



Table 8 summarizes the data used to estimate H_L,acetone-sulfuric acid-

Table 8. Properties at 25 °C used in Eq. 9 to Estimate H_{L,acetone-sulfuric acid}

				Wat	er		73	% Sulfuric Acid
Viscosity, c	p			0.9	5^{I}			11.00 ²
Density, lb				62.2	20^{3}			102.364
Diffusivity,	cm^2/s	· Acetone in Se	olvent	1.2	25			Unknown
Schmidt Nu	ımber, l	N _{SC}		782.	00			40777.00
n	=	0.22;	a	=	100;	s	=	0.5

References:

- Perry's Handbook
- 2. Kirk and Othmer Encyclopedia, Vol. I, p.196
- Perry's Handbook
- 4. International Critical Table
- 5. Tyn, M.T., Culus, W.F.; J. Chem Eng & Data, 20, 3 (1975)

Actually, the value of H_L, the resistance to mass transfer in the acetone-sulfuric acid system can only be estimated by this method because diffusion of acetone into sulfuric acid is not the sole factor. Rather, the absorption of acetone in concentrated sulfuric acid is in reality absorption with chemical reaction. The kinetic reaction factors must play a role. It is believed that the acetone will react rapidly as it reaches the sulfuric acid film. However, very little is known about the kinetic rate constant, its role in the resistance in the liquid film, and the rate of diffusion of the reaction products in determining the liquid film resistance. The data for Othmer and Scheibel (1941) indicted that 74 percent of the overall resistance in the acetone-water system is in the gas phase. With the equilibrium constants in the acetone-sulfuric acid system being much lower than that for acetone-water system (Figure 10), it is believed that for the case of absorption with chemical reaction of the acetone in sulfuric acid, the major resistance to mass transfer will be in the gas phase and that this will approach 100 percent.

The Wilke-Chang equations can be used to estimate the diffusivity of acetone in 73 percent sulfuric acid by Equation 10.

D=7.4E-8
$$\frac{[XM]^{0.5}T}{\mu V^{0.6}}$$
 (10)

Hence, Equation 9, becomes

$$\frac{D_{\text{acetone-H}_2SO_4}}{D_{\text{acetone-H}_2O}} = \left(\frac{M_{\text{H}_2SO_4(73\%)}}{M_{\text{H}_2O}}\right)^{0.5} \left(\frac{\mu_{\text{H}_2O}}{\mu_{\text{H}_2SO_4(73\%)}}\right)$$
(11)

Thus, D acetone-H2SO4 (73 wt %) is calculated to be 6.424 E-06 ft² / hr and HL, acetone-H2SO4 (73 wt %) is 12.64 feet. For acetone-H2SO₄ (73 wt %), Equation 6 becomes Equation 12.

$$H_{OG} = 2.38 + 12.64 \frac{mG}{L}$$
 (12)

Figure 18 shows the correlations of Equations 7 and 12. The estimated H_{OG} for the mixer unit and FAD unit are summarized in Table 7 and the required packed height is also shown. The estimated packed tower height is less for sulfuric acid over water but neither is very large.

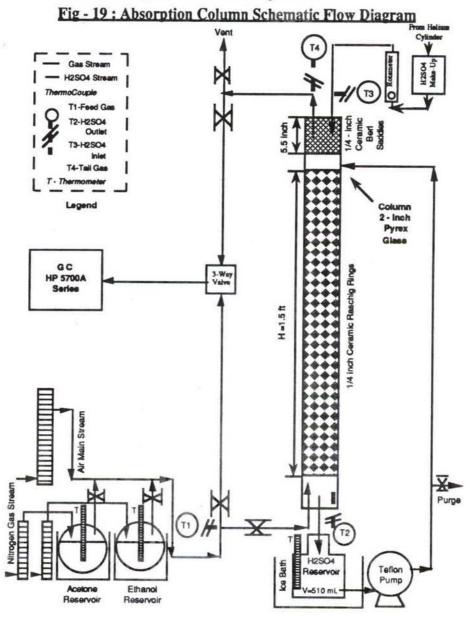
0.5 Acetone-Air-H2SO4 Acetone-Air-H2O Fig-18 : Height of Transfer Unit vs. m G/L (Intercept = 2.38) m G/L 0.2 87 5-9 3-2 ∄,_æ H

Packed Column Absorption Studies

At the request of the research sponsor, a gas absorption experiment was devised for a packed tower with a continuous gas phase containing acetone, and ethyl alcohol in air, and a batch liquid system with recirculating 76 percent and 96 percent sulfuric acid. The concentrations would simulate the air flow from the mixer and the FAD units.

Experimental Apparatus

The same gas chromatograph that was used for the equilibrium studies was used for the absorption studies. The flow diagram is shown in Figure 19.





The gas absorption column was made of 2 inch diameter Pyrex glass pipe packed to height of 1 foot, six inches with 1 / 4 - inch Ceramic Raschig rings. The top of the column was a short section of 1 / 4 - inch Berl Saddle packing, 5.5 inches high. The section was installed for true countercurrent absorption using fresh purge sulfuric acid. Temperatures were measured of the input and output streams with thermocouples. Other temperatures were measured with thermometers. The sulfuric acid reservoir was a glass bottle with a capacity of about 510 ml and was cooled in an ice bath. The recirculating pump was a Teflon Low Flow Diaphragm Pump, Cole - Parmer Catalog Number L - 07088 - 48. The pump speed (or flow) was controlled by Cole - Parmer Series 2630 power supply, variable speed controller, Cole - Parmer Catalog Number L - 02630 - 25. All tubing, fittings, and valves were made of type 316 stainless steel or teflon.

The air to the column was filtered and controlled with a calibrated rotameter with a maximum scale reading equal to 31 liter/min. (Max = 100%) The acetone and ethyl alcohol glass reservoirs were 500 ml 3-neck flasks and flows were metered with rotameters with maximum scale rates of 2 liter/min (Max = 100%) and 6.8 liter/min (Max = 100%) respectively.

The fresh, 76 percent sulfuric acid purge was stored in a reservoir made of 2 - inch Pyrex glass pipe, 8 inches long. The flow was forced into the system by pressurizing the free space of the reservoir with 5 psig of helium gas. The purge was controlled through a rotameter at 1 ml/min and room temperature.

Experimental Theory

The breakthrough curves of amount VOC removed can be developed as a function of time. Since the liquid phase is recirculated, an unsteady state material balance is necessary. The equation is:

Accumulation = Input - Output - Disappearance by Reaction (13) Hence, for acetone, the component balance assuming pseudo first order kinetics is:

$$M \frac{dx_{1A}}{dt} = G_1' y_{1A} - G_2' y_{2A} - k_A x_{1A}$$
 (14)

This equation reduces to

$$M \frac{dx_{1A}}{dt} + k_A x_{1A} = G'(y_{1A} - y_{2A})$$
 (15)

for the dilute system with no purge rate of sulfuric acid.

Similarly, for ethyl alcohol, the component balance is:

$$M = \frac{dx_{1E}}{dt} + k_E x_{1E} = G'(y_{1E} - y_{2E})$$
 (16)

For runs with a sulfuric acid purge, the equation for acetone becomes:

$$M \frac{dx_{1A}}{dt} = G[y_{1A} - y_{2A}] - [L_{1}'x_{1A} - L_{2}'x_{2A}] - k_{A}x_{1A}$$
(17)



Since pure acid is used, x_{2A} is zero, and for dilute systems Equation 17 becomes:

$$M \frac{dx_{1A}}{dt} = G \left[y_{1A} - y_{2A} \right] - L_{1} x_{1A} - k_{A} x_{1A}$$
 (18)

A similar equation can be written for each component, ethyl alcohol, diethyl ether (inlet feed is zero), and water (from air humidity). With proper purge, the transients should eventually disappear and steady state may be achieved.

Experimental Procedure

The air flow was set at 15 liter / min and the nitrogen rates to the acetone and ethyl alcohol reservoirs were set at 150 ml / min and 750 ml / min respectively. The reservoirs were kept at room temperature. The air feed was heated to the desired temperature of 140 $^{\rm O}$ F (60 $^{\rm O}$ F). The feed gas and off gas were analyzed. The sulfuric acid recirculating rate was set at about 100 ml / min. The liquid and gas flow rates were set to avoid flooding and the L / G ratio was in the vicinity of the loading point.

Samples of absorber effluent gas were analyzed over a period time to determine **breakthrough**. For runs with a sulfuric acid purge, the purge rate was about 1 - 2 percent of the recirculation rate. After a few runs, it was noted that the packing began to settle. At this point, the column was inverted to loosen the packing and returned to its original packed height.

Experimental Results

The experimental results of the absorption study are shown in Figures 19 - 21. Figure 19 shows that the humidity in the laboratory air causes the sulfuric acid concentration to decline with time. The relationships are nearly all linear.

Figure 20 shows the percent VOC removed as a function of time for two duplicate runs with recirculating 76 percent sulfuric acid and no purge for acetone. The first traces of acetone appeared in the absorber gas effluent in about two hours. Thereafter, the amount of acetone in the absorber gas effluent increased rapidly and, hence, the percent VOC removed dropped sharply. **Breakthrough**, defined as an acceptable 85 percent removal of the VOC (Jake, 1987), occurred in about 4 - 5 hours. Figure 20 also shows that there was no breakthrough for ethyl alcohol, and also there was no trace of diethyl ether. Figure 21 compares the data with no purge to that with a small purge rate of 1 ml / min (Recirculation rate is 100 ml / min). There was no evidence of acetone in the absorber gas effluent until about 18 hours. Thereafter, the percent removal dropped sharply as acetone began to appear in the absorber gas effluent, and breakthrough occurred in about 21 hours. There was still no evidence of ethyl alcohol nor diethyl ether in the absorber gas effluent.

Figure 22 shows the same results with 96 percent sulfuric acid for a 24 - hour run. There was no trace of acetone, ethyl alcohol, or diethyl ether with recirculation only. Purge acid was not needed during this period.

Observations were made with 76 percent acid indicating that the sulfuric acid became green in color but remained clear. This color was probably due to the corrosion of stainless steel resulting in chromium ions. For 96 percent acid, the color first appeared light yellow (probably acetone reacting with sulfuric acid to form Di Isopropylidene Acetone [Ref. Table 1]), and then became dark brown. The reaction products of the VOC's, acetone and ethyl alcohol, with sulfuric acid were the possible causes. There was same evidence of stainless steel corrosion. The acid had no effect on the glass column, ceramic packing, or teflon parts used in the system. (pump etc.)

The literature (E. I. du Pont de Nemous and Company, Inc.) shows various materials of construction are resistant to 76 percent and 96 percent sulfuric sulfuric acid. Type 304 stainless steel is not resistant except at concentrations greater than 100 percent. However, type 316 stainless steel is resistant at lower temperature to acid concentrations greater than 80 percent.

Discussion of Results

The decline in sulfuric acid concentration on an organics free basis with time, which is shown in Figure 19, results from the humidity of the laboratory air. Humidity considerations will be a major design factor. These calculations are also dependent upon the size of the reservoir. A larger reservoir, would mean a less rapid decline in concentration with time. These data show that a purge rate of sulfuric acid will be necessary. Furthermore, if the concentrations of the purge acid were higher than 76 percent, the recirculating acid concentration can be maintained at a constant value.

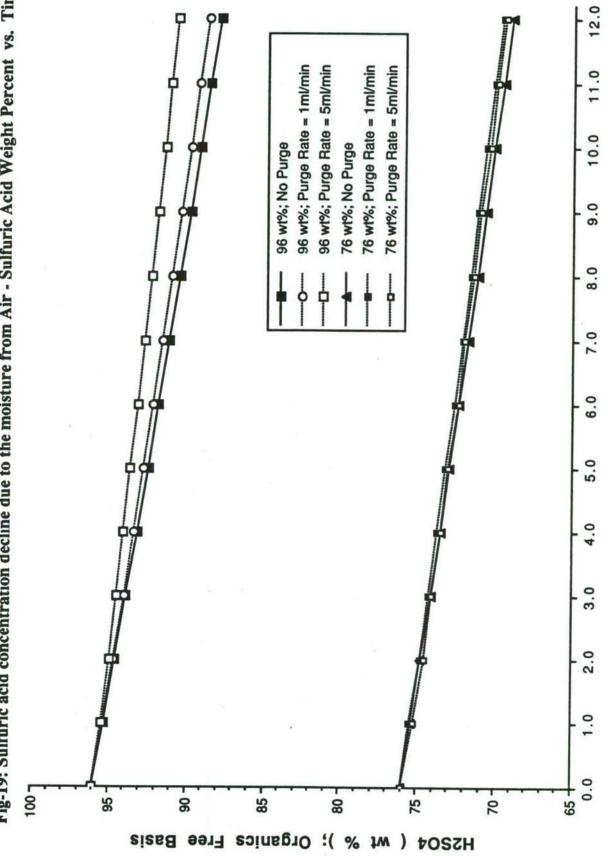
Figure 20 shows that a recirculating 76 percent acid system alone cannot remove acetone sufficiently. However, the sulfuric acid did remove ethyl alcohol completely and there was no trace of diethyl ether in the absorber gas effluent. A comparison of Figure 6 and 7 shows that the equilibrium constant at room temperature for ethyl alcohol is about half that of the acetone. Hence, the ethyl alcohol is held more tightly in the liquid phase than acetone. In addition, the ethyl alcohol may react more rapidly to ethyl sulfuric acid and, hence, held more firmly in solution. Acetone reactions may be slower. Figure 21 shows that a purge rate of 1 ml / min, prolongs the breakthrough time for acetone by a factor of 4 - 5. These breakthrough times are also dependent upon the reservoir size. Higher purge rates or higher concentrations prolong breakthrough.

Figure 22 shows that 96 percent sulfuric acid appears to remove all the acetone and ethyl alcohol for the period of the study. In a totally recirculating system, some breakthrough will eventually occur because the acid concentration will fall, and, hence, the equilibrium constant will rise. These facts will eventually cause acetone to appear in the absorber gas effluent.

In all runs, there was no trace ever of diethyl ether in the absorber gas effluent. In addition, none of the products of reaction appeared in the absorber gas effluent when the GC column was raised to a temperature of about 140 °C from a previous maximum of 110 °C and the retention time was observed to 15 minutes.

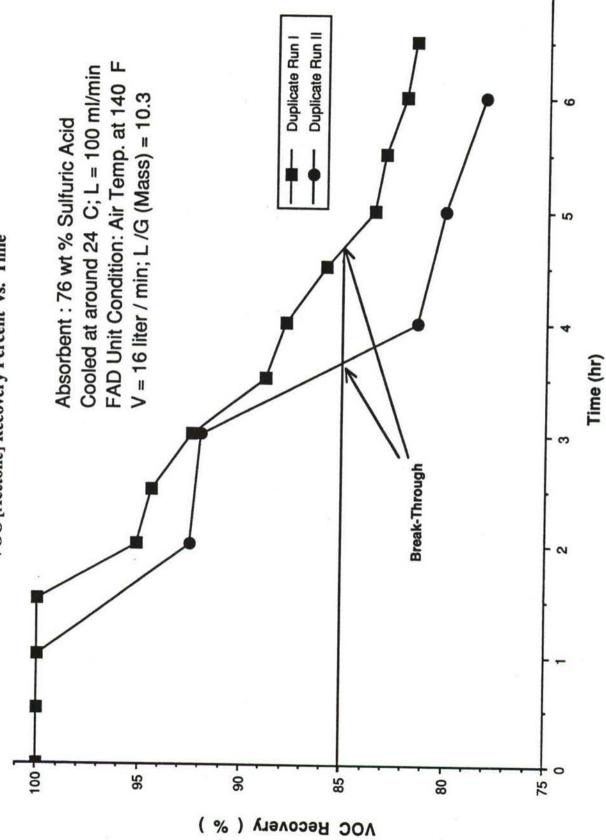
Corrosion and material of construction considerations are important to keep plant investment and maintenance costs low. Type 304 stainless steel is not suitable and it may have been the major cause of the green color observed with 76 percent acid. There was no absolute control on the parts used in the experimental apparatus and, hence, it is possible that some type 304 stainless steel was used. Type 316 stainless steel is suitable in acid strengths above 80 percent by weight at lower temperatures. In the region of 96 percent acid, the temperature can rise to as high as 40 - 60 °C and type 316 stainless steel is still suitable. Suitability is defined as a corrosion rate of less than 0.02 inches per year.

Fig-19: Sulfuric acid concentration decline due to the moisture from Air - Sulfuric Acid Weight Percent vs. Time



Time (hr)

Fig-20: Duplicated Runs in the Absorption Column Using 76 % Sulfuric Acid (No Purge) VOC [Acetone] Recovery Percent vs. Time



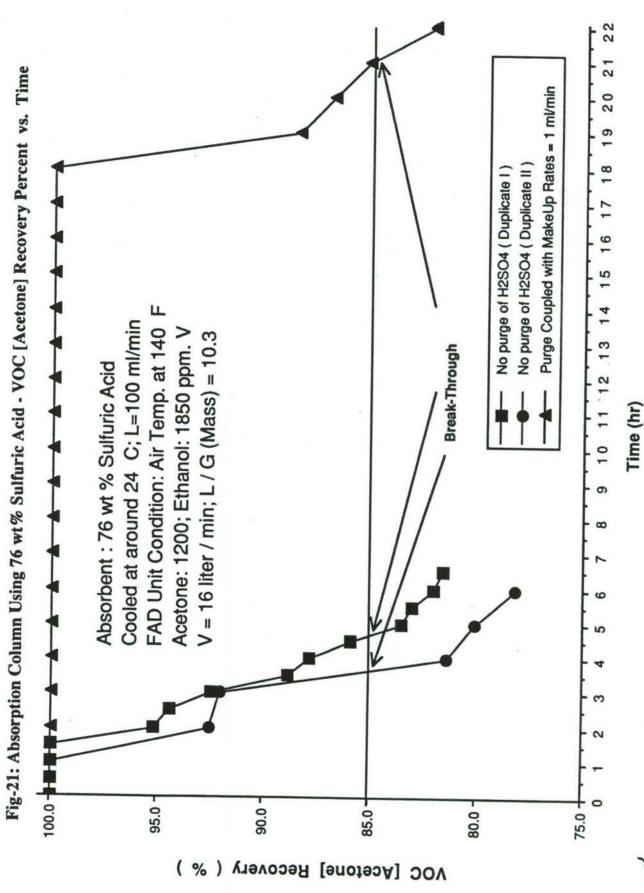
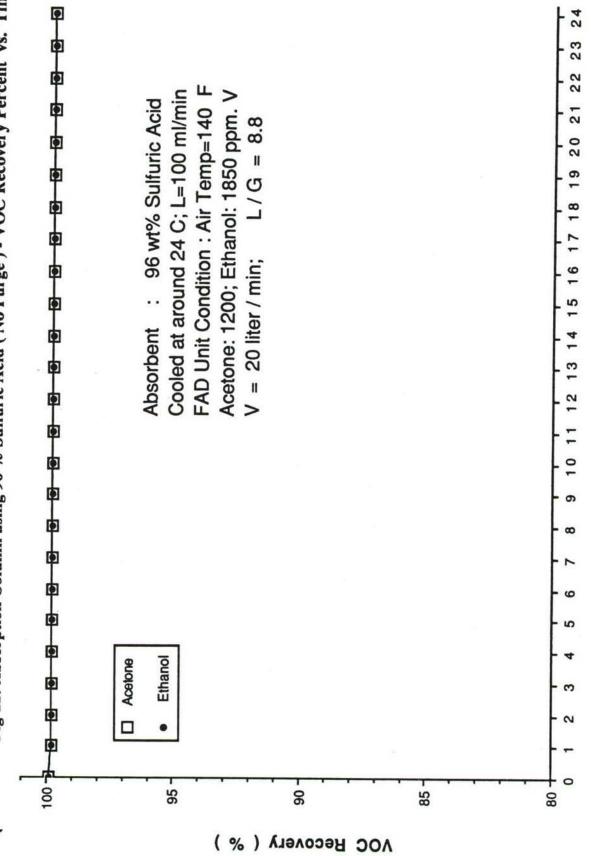


Fig-22: Absorption Column using 96 % Sulfuric Acid (No Purge) - VOC Recovery Percent vs. Time



Time (hr)

Simulation of VOC Removal

The process design of the VOC removal system utilizing recirculating concentrated sulfuric acid requires that a dynamic analysis be made of the acid accumulator, since the mass and energy relationships that describe the acid inventory are by definition time dependent. This is best illustrated by considering the forced air dryer (FAD) effluent air process unit which has a design air flow of 3,000 cubic feet per minute at 140 °F. The following table summarizes the contaminants present in the effluent from the FAD unit.

3,000 cfm of Air at 140 °F Water and VOC Content (From the FAD Unit)

	ppm (Vol)
Water	44,000
Acetone	1,200
Ethanol	1,850
NG	15

A sulfuric acid concentration greater than 90 wt % is sufficient to remove all of the water vapor and at least 85 percent of the acetone, ethyl alcohol and nitroglycerin (NG) VOC's present in the FAD effluent. The design take up of the contaminants by the acid solution is summarized in the following table, and is based on the above removal factors.

3,000 cfm of Air at 140 °F Acid Solution Take-Up

	Lb/hr				
Water	335				
Acetone	25				
Ethanol	31				
NG	1.2				

The circulation rate of the acid solution to be employed in the vapor - liquid contactor is established using as the criteria a pressure drop which will generate good vapor - liquid contacting and hence the realization of the desired removal of the volatile organic compounds from the forced air dryer unit's effluent. The removed material will accumulate with the circulating sulfuric acid.

The minimal volume of acid in the scrubbing system is set by estimating the overall holdup in the major pieces of equipment plus the associated piping. Good design practice dictates that the operating acid inventory in the acid accumulator be sufficient so that the operation of the acid circulation pump and the ancillary equipment consisting principally of an acid heat exchanger will have stable operating characteristics.

Material Balance

The initial design and analysis of the circulating acid system material balance considered the following.

- o The accumulated water will dilute the initial acid charge.
- o The acid concentration will be maintained at a level of 95 wt % using makeup acid coupled with an acid purge.
- o The acid addition and purge will be designed to maintain the minimum acid concentration, and thus the VOC's will not have steady state characteristics.
- o The VOC's in the acid solution will consume negligible quantities of sulfuric acid.

The design analysis of the acid circulation system was accomplished by the development of a simulation model using BASIC for portability and rapid model development. The model used a specified inventory of 2,000 gallons of 96 wt % sulfuric acid. Provisions exist to allow the initial acid inventory to have VOC's present. The minimum acid concentration was set at 95 wt %. This level was established by considering materials of construction versus acid strength. The 95 wt % acid concentration will be maintained using 98 wt % acid as makeup plus an acid purge.

The water - VOC take up by the circulating acid from the FAD air effluent was assumed to be 100 % of the water and a specified 85% removal rate for the VOC's. The model development permits variable water and VOC content in the feed gas as well as variable recovery factors. The material balance associated with the model assumes initial operation with no acid makeup - purge. The dilution of the acid is monitored until the minimum acid concentration is achieved. When the minimum strength acid is reached, makeup acid (98 wt %) coupled with an acid purge stream is used to maintain the specified minimum acid strength. The concentration of the VOC's is continuously monitored during the acid circulation both with and without acid addition - removal.

Using an initial inventory of 2,000 gallons of uncontaminated 96 wt % sulfuric acid, it took 1.0 hour before the circulating acid reached the minimum acid level of 95 wt %. The 95 wt % acid strength was maintained utilizing an 11.5 gpm acid addition rate (98 wt % acid) coupled with an 11.9 gpm purge rate of 95 wt % acid (containing VOC's). The ability to use oleum to maintain the minimal acid level concentration was not included in the model development.



Energy Balance

The energy balance associated with the VOC recovery unit model considered the following issues in accomplishing the process design of the sulfuric acid cooler.

- o The entering air stream is cooled from the entering gas temperature (140 °F) to the specified discharge temperature.
- o The removed water and VOC's are condensed.
- o The condensed water dilutes the sulfuric acid accompanied by a heat of reaction.
- o The makeup purge acid streams are included in the acid solution energy balance.
- o The unsteady state energy balance is used to establish the heat duty associated with the acid cooler under variable load conditions.

The 2,000 gallon acid inventory is initially circulated without acid addition - purge or use of the acid cooler. The VOC removal system operates only for 0.15 hours before the acid inventory experiences a temperature rise of 10 °F from the initial temperature of 80 °F to a maintainable operating temperature of 90 °F. To sustain the operating temperature of 90 °F, 0.76 M Btu / hr must be continuously removed in a heat exchanger. When the acid inventory reaches the 95 wt % level due to water take up, the acid makeup - purge is initiated. Under these circumstances the heat duty associated with the external heat exchanger reduces to the level of 0.56 M Btu / hr because of the addition of cold makeup acid (80 °F) and the removal of energy via the acid purge stream. The two heat removal levels associated with the external acid cooler are essentially constant due to the low level of VOC's in the system.

VOC Buildup in Acid Solution

The continuous circulation of sulfuric acid in contact with the FAD air effluent containing some 3,065 ppm (by volume) of VOC's does not exhibit steady state characteristics. The acid addition - purge is designed to maintain the acid concentration level at the stipulated minimum of 95 wt %. With the water-sulfuric acid steady state material balance established, the other species present in the FAD effluent continue to have an unsteady state behavior. Even considering the VOC's present in the acid purge the VOC's continue to exhibit a buildup in the acid solution. The following table describes the time variation of VOC's (ppm by wt). These data were obtained from the simulation model, and clearly describe a linear relationship with time.

3,000 cfm of Air at 140 °F VOC Buildup in Acid Solution, ppm

				-
	12 hr	24 hr	36 hr	
Acetone	9,440	18,490	27,160	
Ethanol	11,560	22,630	33,250	
NG	460	905	1,330	

The model can thus be used to characterize the VOC content in the total acid inventory with time. With the constraint of a specified minimum acid concentration, the only manipulative parameters available to the process designer is the size of the initial acid charge and the initial loadings VOC's. The above tabular data reflects an initial acid charge 2,000 gallons void of VOC's. Thus the hydrocarbon concentrations can only be reduced by using a larger acid charge or to totally replace the acid with a fresh charge at some predetermined interval.

Conclusions

The conclusions of this study are:

- 1. Using 96 percent sulfuric acid in a gas absorption column can remove acetone and ethyl alcohol, with or without purge.
- 2. Using 96 percent sulfuric acid will prolong breakthrough time.
- 3. Seventy six percent acid is not as effective as ninety six percent acid.
- 4. The humidity in the air will be a major factor in the system design.
- 5. A continuous system using 96 percent sulfuric acid can be designed to remove effectively all of the acetone and ethyl alcohol from the air leaving the mixer units and the FAD units.
- 6. The proper choice of acid strength and temperature can result in use of cheaper materials of construction to keep plant cost down.

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Nomenclature

D = diffusivity, m^2/hr or ft^2/hr

D = $diffusivity, cm^2 / s, Eq. 10$

G = gas flow rate, kg moles / m², hr or lb moles / ft², hr

H_G = individual height of a transfer unit, gas phase, m or feet

H_L = individual height of a transfer unit, liquid phase, m or feet

HOG = height of a transfer unit, m or feet

k_xa = individual mass transfer coefficient, liquid phase,kg moles / hr · m³ ·m.f. or

lb moles / hr, ft3, m.f.

k_va = individual mass transfer coefficient, gas phase,kg moles / hr · m³ ·m.f. or

lb moles / hr 'ft3 'm.f.

Kya = overall mass transfer coefficient, kg moles / hr · m³ ·m.f. or lb moles / hr · ft³ ·m.f.

L = liquid flow rate, kg moles / m², hr or lb moles / ft², hr

M = molecular weight of solvent, Eq. 10

 μ = viscosity, cp, Eq.10

 μ = liquid viscosity, kg/m-hr or lb/ft-hr

N_{OG} = number of transfer units

 N_{SC} = Schmidt Number = $\mu/\rho D$

T = temperature, OK, Eq.10

V = molar volume of solvent (acetone = 77.5 ml/gmole), Eq. 10

 ρ = liquid density, kg/m³ or lb/ft³

X = 2.6 for water as an associated solvent, Eq. 10

x = mole fraction, solute in the liquid phase

y = mole fraction, solute in the gas phase

y* = equilibrium mole fraction in the gas phase

Z = packed height, m or ft

Subscript

- entrance to column for gas phase
 A. Acetone
- leaving from column for gas phase
 Ethyl Alcohol

TREATMENT OF PROPELLANT PRODUCTION WASTEWATER CONTAINING DNT USING EXPANDED BED GRANULAR ACTIVATED CARBON ANAEROBIC REACTORS

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ABSTRACT

Dinitrotoluene (DNT) is used in the production of propellants enters the wastewater stream through several operations including water dry, wet screening and solvent recovery. Regulatory levels for this compound have been set at 114 μ g/L in the NPDES permit for Radford Army Ammunition Plant (RAAP). existing wastewater treatment facility is unable to meet these new levels at all times. Hercules, Inc. conducted a study at RAAP (Removal of DNT from RAAP Wastewaters, PEI Associates Subcontract No 897-88) which assessed a number of technologies for removal of DNT, including biodegradation, UV/ozone oxidation and granular activated carbon (GAC) adsorption. The results from the GAC study were inconclusive because the adsorptive capacity as determined by isotherm tests differed dramatically from that obtained in the column flow-through study. Such a phenomenon suggests that biodegradation on GAC may be occurring, and if so, this is a process by which the DNT can be degraded while at the same time providing a buffer for fluctuations in DNT concentration. Further characterization of the RAAP wastewater indicated that excesses of other easily biodegraded substrates would likely cause any biological reactor to operate in the anaerobic mode.

Use of anaerobic expanded bed GAC reactors is an emerging technology for difficult-to-degrade organics. The GAC provides a storage place (through adsorption) for times when the DNT concentration is in excess of the bacterial capacity to assimilate, and then desorbs the DNT when concentrations decrease, maintaining the DNT feed to the bacteria. If successful, this technique will provide a method to treat DNT at the source without requiring the regeneration of GAC. The use of the GAC as a buffering mechanism and support surface for the bacterial film will also decrease requirements for operator intervention during variations in flow and concentration.

Introduction

Dinitrotoluene (DNT) is a contaminant which is being controlled at ever more stringent levels. As a component of propellants, it is found in the wastewaters from production at the Radford Army Ammunition Plant (RAAP). A major point source contributor is the water-dry operation, in which solvents are removed from the propellant. This is a batch process in which DNT,

ethyl ether and ethyl alcohol enter the waste stream. Grab sample analysis at one manhole near these operations indicates that DNT levels can reach 75 mg/L, in conjunction with ethanol (495 mg/L and ether (9.3 mg/L).

A study of various mechanisms for DNT removal was conducted¹ which evaluated advanced oxidation (ultraviolet light with ozone), biodegradation and granular activated carbon adsorption. Advanced oxidation processes are well established for aromatics² and DNT in particular³. DNT is a relatively non-polar organic for which granular activated carbon is also effective⁴. Biodegradation has also been suggested₁ but not to complete ring cleavage. However, there was a major discrepancy between adsorption isotherms and column flow-through using the wastewater in question¹. Detailed review of the data generated in the initial study¹ suggested that biodegradation was a major factor.

Parameters for column studies of GAC removal of were initially based on isotherm results¹, but breakthrough was not observed as expected. In the column study, the GAC capacity appeared to be at least 50% greater than that observed in isotherm (batch) studies. In their evaluation, only adsorptive capacity was considered. However, it is well established that GAC is an excellent surface for bacterial attachment⁵, and that for compounds that are both adsorbable and biodegradable, GAC provides a "storage" buffer for peaks of influent concentration which are reflected in greater rates of bio-conversion, e.g., gas production rates for anaerobic systems⁶, that lag behind influent loading. A removal rate from column studies which is substantially larger than that from isotherm studies strongly suggests biodegradation as a mechanism.

Biodegradation and biotransformation of DNT has been evaluated using fungi⁷ and bacteria⁸⁻¹⁰. Several pathways and transformation products have been identified including nitroso-compounds⁸. Therefore, the potential for undesirable by-products of the biodegradation must also be assessed. These compounds may be removed by the GAC, or they may pass into the effluent. If GAC is the removal mechanism, then the capacity exhaustion for the by-products may be the limiting step in GAC service life.

Results

Influent concentrations of DNT and associated organics were based on data from the initial study¹. Data on the sulfate concentrations were unavailable at the outset of the study, so two columns of combined adsorption/biodegradation were initiated. One was set up to favor a low-sulfate culture of bacteria, and the other was set up to favor a sulfate reducing bacterial population. Subsequent samples obtained from RAAP indicated low concentrations of sulfate, so the sulfate was eliminated from the feed stock and that column was used to evaluate reduction in hydraulic retention time. The other column was also modified after analysis of the RAAP wastewater. Lower than expected concentrations of ethanol and ether were found in the sample, so those concentrations were



reduced in the second column to one-eighth (12.5%) of that in column one.

Two expanded-bed contactors, each charged with one kilogram of GAC (Calgon F-400), were acclimated to a feedstock of ethanol for one month. Seed bacteria were obtained from methanogenic cultures at the U.S. EPA Test and Evaluation Facility. All column operation was conducted at 35 °C to favor methanogens. Buffers, salts and nutrient solutions were fed in conjunction with ethanol (and later feedstocks). The composition of these solutions are shown in Tables 1 through 3.

TABLE 1. STOCK TRACE SALT SOLUTION*

 Component	Concentration (g/L)			
Ammonium Molebedate	2.08			
Sodium Borate	1.15			
Nickel Chloride	3.00			
Manganese Chloride	4.74			
Cobalt Chloride	2.86			
Zinc Chloride	3.27			
Copper (II) Chloride	2.05			

*These components must be added in the order they are listed.

TABLE 2. STOCK SALT SOLUTION*

=======	Component	Concentration (g/L		
	Trace salt solution	33.1 ml/L		
	MgCl ₂ * 6H ₂ O	8.13		
	NaH ₂ PO4 * H ₂ O	8.28		
	KH ₂ PO4 * H ₂ O	13.6		
	NH ₄ Cl	17.0		
	CaCl ₂ * 2H ₂ O	5.86		

* Same note as listed in Table 1.

The reactor volume is eight liters, and the expanded bed occupies approximately half of the reactor volume. Synthetic wastewater samples were fed initially at a rate of 1.5 L/day, with the rate being doubled at day 109 to 3 L/day and doubled again at day 186 to 6 L/day yielding a GAC contact time of 16 hours from day 186 onward. Figure 1 shows the variation of DNT in the feedstock over the first 300 days of the study. After the acclimation period, DNT was rapidly loaded using overall applied concentrations of up to 700 mg/L. Finely ground DNT was applied through a sidearm in the reactor to increase the applied concentration beyond the

TABLE 3. STOCK VITAMIN SOLUTION*

Component	Concentration (g/L)		
 p-Aminobenzoic Acid	0.01		
Biotin	0.0039		
Cyanocobalamin (B12)	0.0002		
Folic Acid	0.0039		
Nicotinic Acid	0.01		
Pantothenic Acid	0.01		
Pyridoxine Hydrochloride	0.02		
Riboflavin	0.01		
Thiamin Hydrochloride	0.01		
Thioctic Acid	0.01		

^{*} Same note as listed in Table 1.

Figure 1 also shows the effluent concentrations for DNT and diaminotoluene (DAT). The concentration scale for DNT and DAT are shown on the right side of the graph, and indicate that the concentration for both compounds remained under 1 mg/L with the exception of one excursion to 25 mg/L for DAT around day 240. 2 shows the cumulative loading of DNT versus the breakthrough concentrations. At the time these data were collected the loading had exceeded 600 mg/g of GAC without appreciable breakthrough of DNT or DAT.

Figure 3 shows the chemical oxygen demand (COD) balance for the column without sulfate addition. COD is expressed as effluent and effluent plus gas, to show the close relationship between the influent concentrations and overall conversion. The results indicate that the effluent remains relatively low throughout the experimental period, but the addition of the amount converted to methane suggests that near complete biotransformation is occurring, rather than substantial adsorption. Results obtained for the column with initial sulfate additional were essentially the same as those shown here.

The extraction method used to analyze for DNT and DAT also has the capacity to detect other compounds which are potential byproducts. Although a detailed evaluation of by-products has not been conducted in this study, the only compounds found to date have been DNT and the compounds from reduction of one or both nitro groups to amino groups (e.g., DAT).

Discussion

The bench scale tests of an anaerobic expanded bed GAC contactor have been quite positive to date. Very little breakthrough of DNT or DAT has been observed. Large variations in the influent concentration (from 40 to >700 mg/L, see Figure 1), have not been accompanied by substantial breakthrough of DNT or DAT. The overall COD balance indicates that the majority of the influent is being converted to methane gas. This large rate of conversion and small rate of DAT formation indicates that DNT is undergoing ring cleavage, i.e., complete biodegradation.

The tests conducted in this study were patterned after the major source of DNT at RAAP, i.e., the "water-dry" operation in which excess solvents are removed from the propellant. Treatment of wastewaters from the "water-dry" appear to be well suited for anaerobic GAC contactors. DNT is a compound which is both adsorbable and biodegradable, and is accompanied by relatively high concentrations of other highly biodegradable compounds (ethanol and ether) in the wastewater. GAC can act as a buffer for the liquid phase concentration of DNT, effectively cutting off peaks in concentrations which the slow-growing methanogens may not be able to handle.

Many questions remain to be answered regarding the use of expanded bed anaerobic GAC reactors for removal of DNT at the source in RAAP's industrial facilities. Synthetic wastewater has been used because of difficulties in acquiring and handling the actual wastewater off-site, and only one type of propellant wastewater has been simulated. Arrangements are underway to transport one of the reactors to a laboratory facility at RAAP so that actual wastewater can be batch fed on a daily basis. The lower limit on contact time is also being investigated, to determine operating conditions for a long term pilot demonstration. However, the success shown to date is very encouraging, and expanded use of this technique to other high strength wastes composed of adsorbable and biodegradable materials.

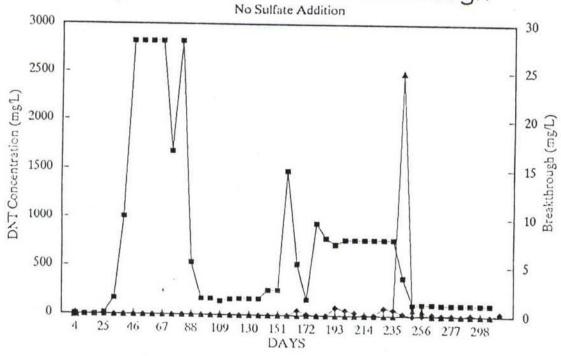
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Figure 1: Column A Breakthrough



__ DNT Influent __ DNT Effluent __ DAT Effluent



Figure 2: Column A Loading and Breakthrough

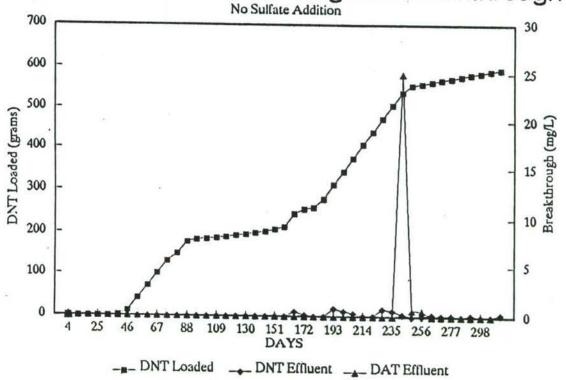
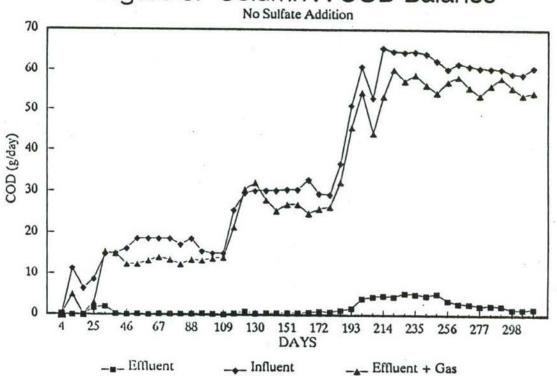


Figure 3: Column A COD Balance



Enzymatic Denitration of Nitrate Ester Wastes: Culture Selection

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Background

As a result of recent concerns for our environment, it has become clear that current technologies for treating toxic organic effluent components have limited capabilities. To meet ever more stringent effluent standards, it is imperative that more efficient and cost effective technologies be developed. In our laboratories, we are exploring such an advanced technology - the use of enzymes for treating toxic wastes (Coppella et al. 1990; Rowland et al. 1991; Smith et al. 1992; Sun et al. 1992). For this study, the overall objective is to examine the use of enzymes for treating nitrate ester wastes. To understand why we believe enzymes may be effective for treating nitrate ester wastes, it is useful to first consider current physical, chemical and biological approaches for treating nitrate ester wastewaters.

The physical treatment technology of choice for removing nitrate esters from effluents is activated carbon adsorption. Activated carbon adsorption does not degrade the nitrate esters, these chemicals are simply moved to another phase. Subsequent treatment (e.g. incineration) is required for ultimate disposal.

Chemical methods for treating nitrate ester wastes (either alkaline hydrolysis or alkaline sulfite treatment) suffer from the problem that large amounts of chemicals are used and that these added chemicals must be subsequently treated before discharge. Thus chemical methods, although destroying the nitrate esters are essentially a trade-off of one waste problem for another - albeit lesser - problem.

The treatment method currently receiving the most attention is biological treatment involving populations of viable microorganisms. Microbiological treatment has three very appealing advantages: (1) it is efficient for removing wastes from dilute solutions; (2) it is inexpensive; and (3) it can result in the complete oxidation (i.e. mineralization) of organics to carbon dioxide and water. Thus when it works, microbiological treatment functions as an incinerator operating in simple equipment, at ambient conditions and with dilute aqueous solutions. Thus microbiological treatment is the dream solution to organic effluent problems. Unfortunately, microbiological treatment suffers from one major problem - it has often been observed to be operationally unstable. Because microbiological treatment has not reliably performed in practice, it has generally not been accepted for the routine treatment of toxic organics in industrial effluents.

With respect to nitrate esters, laboratory studies have demonstrated that microbiological methods are potentially capable of degradation (Wendt et al. 1978; Ducrocq et al. 1989, 1990). Again, however, the reliability of microbial treatment has been questioned (Wyman et al. 1984).

Enzyme-based treatment of nitrate-ester wastewaters

Because of the difficulties of treating nitrate ester wastes with traditional technologies, we have begun to investigate an alternative technological approach - the use of enzymes. It must be noted that not all wastes can be effectively treated using enzymes nor are all enzymes appropriate for waste treatment. For an enzymatic approach to be appropriate, we believe the four requirements in Table 1 must be met (Payne et al. 1989). Recognizing that enzymes are only able to mediate a single or a small number of reactions, this reaction must be useful if an enzymatic treatment approach is to be appropriate. Examples of useful reactions are those which detoxify or break recalcitrance of a waste.



The second entry in Table 1 states that the cosubstrate requirements of the enzyme must be simple. Although many enzymes in nature require complex biological cosubstrates (e.g. ATP or NADH) such cosubstrate-requiring enzymes are seldom practical for industrial or waste treatment applications. Thus most studies have focused on enzymes that require such simple cosubstrates as water (Munnecke 1980; Basher et al. 1992), oxygen (Atlow et al. 1984; Shuttleworth and Bollag 1986) and hydrogen peroxide (Klibanov and coworkers 1980, 1981; Aitken 1989). Interestingly, Mellor et al. (1992) recently reported an immobilized enzyme system for converting groundwater nitrate to N2. Although the enzymes used in their study typically utilize NADH, the requirement for reducing equivalents was met by co-immobilizing an electron-carrying dye and using an electrical current. This work suggests that even enzymes which mediate oxidation-reduction reactions may be appropriate candidates for waste treatment. The final two entries in Table 1 consider the operational performance of the enzyme and must be viewed in terms of competing alternative technologies.

Table 1. Requirements for an enzyme to be appropriate for treating toxic organic waste components.

- 1. Reaction must be useful
- 2. Cosubstrate requirements must be simple
- 3. Enzymatic activity must be appropriate
- Stability must be appropriate

With respect to the enzymatic treatment of nitrate ester wastes, we believe that an enzyme capable of removing the nitrates from the carbon skeleton of the nitrate esters would meet the first requirement in Table 1. Denitration of the nitrate esters would likely reduce the toxic and explosive character of these compounds and also make these compounds more amenable to subsequent microbiological treatment. Thus denitration of the nitrate esters would be likely to result in products capable of being readily degraded by standard activated sludge treatment operations. Despite the desirability of denitrating enzymes, there were two potential problems when we began this study. The first problem was that although microbial denitration of nitrate esters has been observed, there are no reports to our knowledge describing the enzymes involved. Thus the first task in this project was to identify candidate enzymes for denitrating nitrate esters.

The second potential problem was that enzymatic denitration of nitrate esters may not necessarily meet the second requirement of Table 1 - that is denitration may not be a simple hydrolytic denitration but rather more complex, cosubstrate-requiring pathways may exist. There are several reports in the literature concerning the microbial denitration of organ-nitro compounds. Nitroaromatics appear to be denitrated by two distinct pathways (see Zeyer and Kearney 1984; Spanggord et al. 1991; Oren et al. 1991). One "denitration" path involves a series of reductions to yield an aromatic amine which may be subsequently deaminated. This path almost certainly requires complex, cell-generated reducing cosubstrates (e.g. NAD(P)H) (Schackmann and Muller 1991). The second path is oxidative and has also been reported to require the complex cosubstrate NAD(P)H (Spain et al. 1979). The denitration of nitroalkanes was also studied (Porter et al. 1972; Porter and Bright 1977; Kido et al. 1975; 1976; 1978; Kido and Soda 1976; Dhawale and Hornemann 1979). From these studies it appears that oxidative enzymes are capable of denitration of nitroalkanes, and that these enzymes do not have complex cosubstrate requirements. Finally, reports on microbial denitration of nitrate esters are limited. However, these reports have suggested that either hydrolytic or oxidation/reduction routes may be involved



(Wendt et al. 1978; Ducrocq and coworkers 1989, 1990). In summary, it appears that denitration of nitrate esters may involve more than a single route, and that there may be enzymes available in nature which can remove the nitrate groups without requiring complex cosubstrates. Thus, in this work we attempted to select for microorganisms capable of denitrating nitrate esters through routes which are likely to involve a single or small number of enzymatic steps which have simple cosubstrate requirements.

Screening for Cultures Capable of Denitration

Traditionally, screens to identify microorganisms capable of treating an organic waste component have been targeted at identifying microbes capable of utilizing the toxic organic as a source (often sole source) of carbon and energy for microbial growth. Such screens are appropriate when the goal for microbial treatment is to achieve complete mineralization of the organic component. Although complete mineralization is an ideal, it has been difficult to achieve this ideal in practice. Since our work is focussed on selecting for organisms containing enzymes capable of denitrating nitrate esters, we attempted to develop screens consistent with this goal.

The first screening approach was targeted at identifying microorganisms capable of utilizing nitrate esters as a sole source of nitrogen. In this approach we provided sufficient carbon and energy sources (e.g. by adding carbohydrates) while limiting nitrogen such that the nitrate esters were the sole source of nitrogen. Only organisms capable of accessing the nitrogen from these esters should be able to grow in the screen. The rationale for this approach is that the first step to accessing the nitrate nitrogen may be a simple hydrolytic denitration reaction. Our rationale for this first screening approach is supported by results from Wendt et al. (1978) in which they observed a 53.6 % decrease in glycerol trinitrate concentration when this nitrate ester served as the sole nitrogen source for mixed cultures.

In contrast, only 3.1 % glycerol trinitrate was removed when it served as a sole carbon source.

The second screening approach was targeted not to the nutritional capabilities of the nitrate esters but rather to the toxicity of these compounds. In this approach, sufficient nutrients (both carbon and nitrogen) were be provided for growth, however, high concentrations (up to 1,000 mg/L glycerol trinitrate) of the nitrate esters were incorporated into the medium. Our rationale here was that only organisms capable of detoxifying the nitrate esters would be able to grow under these conditions and that detoxification would possibly result from a simple hydrolytic denitration.

To select for microbes, we obtained soil and sediment samples known to have been exposed to nitrate ester contaminants. After subjecting these samples to the above-mentioned screens, 56 isolates were obtained. These isolates are currently being studied to characterize their abilities to denitrate glycerol tri- and mono-nitrates.

Conclusions

We believe that enzymatic methods may offer potential benefits for treating nitrate ester wastes. If enzymes were available which could denitrate nitrate esters, these enzymes could be used to reduce the toxicity, the hazard and the recalcitrance of nitrate ester wastes. Since enzymes capable of denitrating nitrate esters are not currently known, we developed screens and selected soil and sediment samples with the goal of identifying cultures with appropriate denitrating activities. From this selection we have 56 isolates in our culture collection and these isolates are being examined for their ability to denitrate glycerol tri- and mono-nitrate.

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DEVELOPMENTS IN THE RECOVERY AND CONCENTRATION OF SPENT SULPHURIC ACID

Iain Smith CHEMETICS International

INTRODUCTION

Spent sulphuric acid has traditionally been treated or disposed of in a number of different ways including:-

- disposal to water sources (rivers, oceans, deep wells)
- neutralisation with subsequent disposal or storage of gypsum
- utilisation in other processes e.g. fertiliser production
- reprocessing via concentration or regeneration

With the introduction of increasingly stringent environmental legislation in many countries stimulated by the various "Green Movements" the first three options listed above are becoming unacceptable. Therefore, attention is becoming focused on means of reprocessing spent sulphuric acid for recycle or resale.

Techniques which are widely used for the recovery of spent sulphuric acid include the following:

- (1) Submerged combustion (e.g. Chemico concentrator)
- (2) Atmospheric concentration by indirect heating (e.g. cast iron pots)
- (3) Vacuum concentration (e.g. Chemetics process)
- (4) Thermal decomposition with acid regeneration (e.g. Stauffer Process)

None of these can be regarded as a universal panacea for all types of spent acid and all of the processes individually may suffer from a variety of drawbacks including high energy requirements, materials of construction difficulties, environmental concerns, insufficient purification of the acid and inability to cope with acids containing inorganic contaminants.

This paper discusses the current situation in spent acid recovery from the perspective of Chemetics' technology. Sections are devoted to the continuing applications of the existing denitration and vacuum concentration technologies

both in new installations and plant retrofits; the new generation vapour phase technology both for inorganic and organic contaminated acids and the developing atmospheric concentration technology based on SARAMETR as a material of construction. Particular emphasis is given to the importance of pilot plant studies in the application and development of all these technologies.

Existing Technology

Chemetics' existing technology comprises nitric acid concentration (NAC), spent acid denitration (DEN) and sulphuric acid concentration (SAC). Sulphuric acid concentration is performed in multi-stage glass-lined steel and tantalum thermosiphon evaporators typically from 70% strength to strengths up to 96%. Chemetics have now installed 14 such facilities and more than 2 x 106 TPA of sulphuric acid is processed worldwide in Chemetics' plants, the largest having a capacity of 1000 TPD.

However, even in this well established field there are noticeable trends. Historically, waste acid recovery facilities have usually been installed in conjunction with a new facility, typically a nitration process. This remains a strong market as typified by the acid concentration units which are an integral part of the Chemetics' nitrobenzene process. Changing environmental and economic circumstances are providing new opportunities for even conventional technology viz:

- retrofits of spent acid recovery units to plants where the previous method of acid disposal has been eliminated;
- (ii) applications for weak acid concentration;
- (iii) combination with other waste acid technologies to provide an optimum solution in either retrofit or new plant applications;
- (iv) applications to spent acids from processes other than nitration.



Retrofit Applications

Many producers have been able to dispose of spent acid either by use in other applications (e.g. fertiliser production) or via discharge to water sources. Changing economic and/or environmental requirements are eliminating these options and producing new opportunities for suppliers of spent acid recovery plants. Recent examples are a 2-stage concentrator built for a large chemical company in Italy, (see Figure 1) to reconcentrate spent sulphuric acid from strong nitric acid manufacture and a similar unit constructed for a U.S. corporation in Mississippi, (see Figure 2) to reprocess spent acid from a nitration. The latter photograph is interesting in that it shows the new 2-stage concentrator in the foreground whilst in the background can be seen the vacuum concentrators which are integral to the Chemetics' adiabatic benzene nitration process installed earlier.

Weak Acid Concentration

Until recently Chemetics spent acid recovery technology had been applied almost without exception to spent acids at around 70% strength. There was little incentive for manufacturers, particularly in North America to consider recovery and recycle for weaker acids. However, increasingly severe environmental regulations are now making the recovery of even weak acid mandatory.

As a recent example, Chemetics have completed a contract with a major U.S. chemical company for the design and equipment supply of a 3-stage vacuum concentration unit to concentrate spent acid from 8% to 50%. Operating at this low strength range, of course, allows the designer the opportunity to utilise the benefits of multiple effect evaporation to reduce energy requirements.

Technology Combinations

A further developing market is the application of combinations of existing technologies, either as a retrofit or for a new installation, to provide effective and economic solutions to waste acid problems.

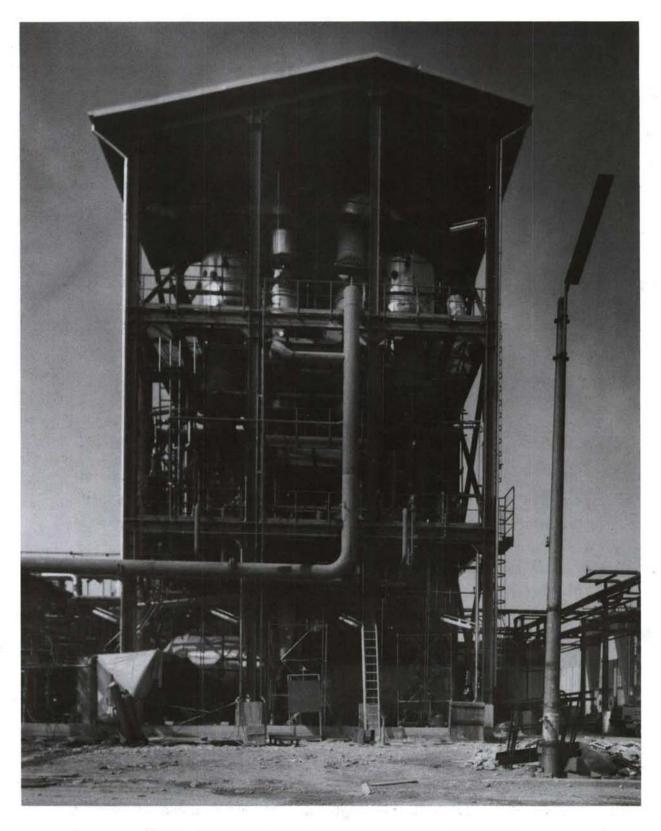


FIG.1: 2-STAGE ACID CONCENTRATOR IN ITALY



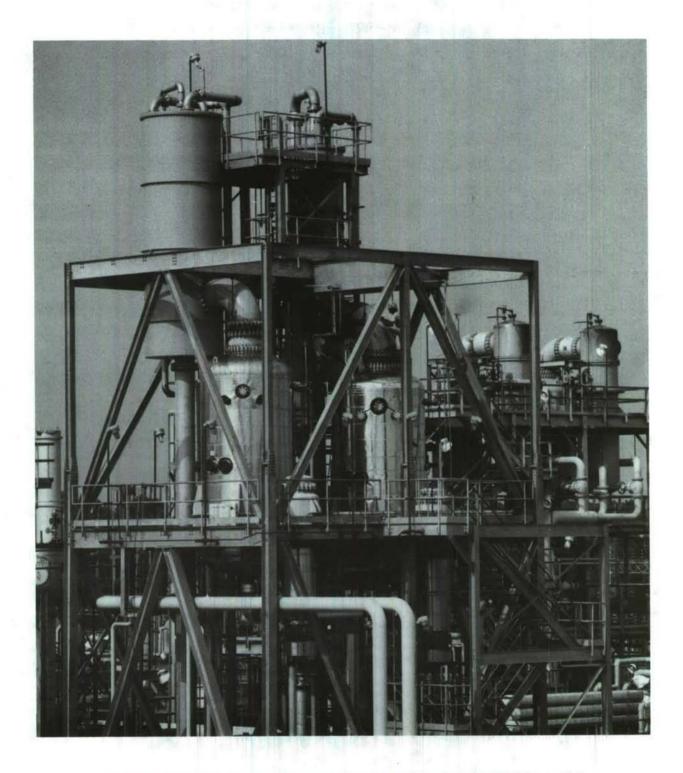


FIG. 2: VACUUM CONCENTRATION UNITS IN MISSISSIPPI, U.S.A.

FOREGROUND: BACKGROUND:

NEW 2-STAGE UNIT

INTEGRAL WITH CHEMETICS 2-STAGE UNIT NITROBENZENE PROCESS



One recent example concerns a client who for many years has utilised a Chemico submerged combustion concentrator to concentrate nitration waste acid for recycle. However, due to the mode of operation of the Chemico concentrator volatile organic compounds present in the spent acid were discharged to the atmosphere from the stack of the concentrator, a practice now regarded as unacceptable. The client wished to retain the Chemico concentrator whilst reducing the emissions to acceptable levels.

After extensive pilot plant testing, Chemetics designed a stripping column for location between the nitration plant and the concentrator. The stripping column removes the majority of the volatile organics such that the stack discharge from the concentrator now meets all emissions criteria. In addition, the organics are recovered as an overheads stream from the stripping column and recycled to the nitration.

Non-Nitration Spent Acid

A further example of combining technologies and, simultaneously, applying spent acid recovery to acids from non-nitration processes concerns the treatment of spent acid from methyl methacrylate (MMA) manufacture.

The conventional technique for recovering MMA spent acid is via regeneration i.e. burning of the acid in a furnace at 1000°C to produce sulphur dioxide with subsequent conversion to sulphuric acid in a conventional acid plant. It was known that some processes included a preconcentration step in order to reduce overall energy costs, but that the preconcentration step resulted in organic emissions to the atmosphere.

Chemetics therefore carried out a comprehensive pilot plant programme to establish whether vacuum concentration would be a suitable technique for preconcentration. The conclusions were as follows:

It was established that the quantity of water which was optimum for recycling to the front end MMA process could readily be removed by vacuum concentration thus reducing the overall process water requirement.



- 2 It was shown that this said quantity of water contained a significant concentration of valuable, recyclable organic compounds.
- The reduction in the quantity of water passing forward to the decomposition furnace results in a significant energy saving.

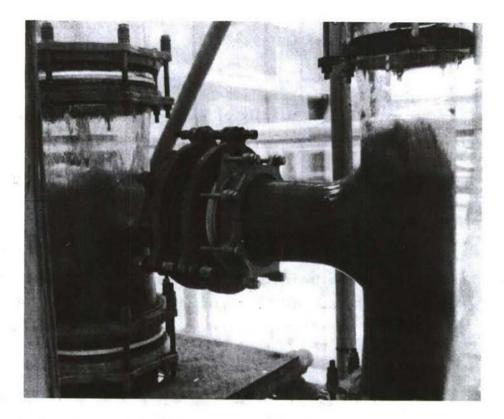
As a result of this successful development, Chemetics are now involved in two projects with one client for the treatment of MMA spent acid via vacuum preconcentration followed by decomposition to sulphur dioxide and subsequent conversion to sulphuric acid. Chemetics are supplying the preconcentration and acid plants with Rhone Poulenc designing the decomposition stage.

Chemetics' ability to pilot the preconcentration step was a major factor in the award of these two projects. Chemetics has made a significant investment in pilot facilities in both Ontario and Quebec and is now able to simulate all of its' waste acid technologies on both the bench and pilot scales.

Pilot plant simulation is important not only to obtain chemical engineering data, but also to establish safe operating guidelines. This is well illustrated in Figure 3. Figure 3A shows the separator vessel of the pilot plant vacuum concentrator operating under design conditions on a spent acid as established by previous bench scale trials. Figure 3B shows the onset of severe foaming on the same spent acid as the process operating pressure and, hence, temperature were raised.

New Generation Technology

The Chemetics' vapour phase process for the treatment and recovery of titanium dioxide waste acid has been described previously. Essentially the process requires complete evaporation of the feed acid at conditions which minimise any breakdown to sulphur dioxide. Metal sulphates are removed in the vapour phase and a concentrated acid product is obtained by partial condensation of the vapours. Chemetics have recently completed a 2 year operation of a 110 TPD pilot plant for TiO₂ waste acid recovery¹.



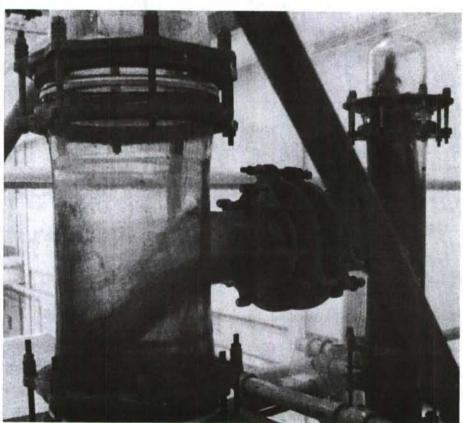


FIG. 3: PILOT PLANT VACUUM CONCENTRATOR SEPARATOR VESSEL: MMA SPENT ACID



It is now becoming apparent that this technology may have other applications far beyond TiO₂ waste acid recovery to a range of spent acids:

- other waste acids containing inorganic contaminants;
- organic containing acids not amenable to treatment via conventional liquid phase technology;
- 3 acids containing a mix of organic and inorganic contaminants.

In order to more fully investigate these possibilities Chemetics has recently constructed a pilot plant at its' laboratory in Quebec (see Figure 4). Preliminary experiments are performed on a bench scale unit to establish whether the acid is suitable for treatment prior to pilot scale experiments.

Inorganic Contaminated Acids

The most obvious extension of the TiO₂ waste acid recovery technology is to other spent acids containing only inorganic contaminants. Chemetics are currently pursuing an active bench scale experimental programme to develop this technology for other inorganically contaminated acids.

Organic Contaminated Acids

There are many organically contaminated acids which are not amenable to treatment via conventional liquid phase processes (vacuum concentration et al) and can only be recovered by decomposition and regeneration. This is usually because the acid is so heavily contaminated that no effective, economic liquid phase process exists to give a clean, concentrated product. An example of such an acid is spent acid from the sulphonation industry which may contain up to 5% of organic contamination.

However, some relatively lightly contaminated acids may also be unsuitable for conventional treatment as the source process is so sensitive to contaminants that close to virgin quality acid is required for recycle.

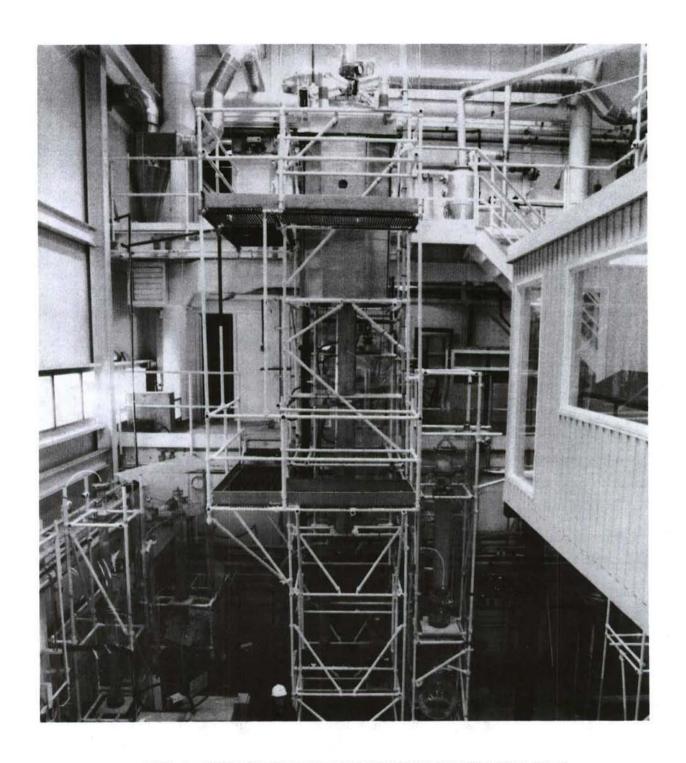


FIG. 4: VAPOUR PHASE ACID RECOVERY PILOT PLANT

Vapour phase technology is a more economic means of treating such acids than by decomposition/regeneration, if it can be established that organic contaminants can be successfully oxidised in the vapour phase at conditions which do not cause significant acid breakdown to sulphur dioxide.

Chemetics are now carrying out a major programme of bench and pilot scale trials to establish the criteria for successfully treating a range of organically contaminated acids. Thus far data has been obtained for acids from the plastics, explosives, petroleum and specialty chemicals industries. Results to date indicate that in all cases the organic contaminants can be oxidised at conditions where no significant decomposition of the acid to sulphur dioxide occurs.

Acids Contaminated with Organic and Inorganic Components

On many sites which manufacture specialty chemicals/dyestuffs numerous small streams of spent acid are produced from a variety of multi-product batch operations. These may amount to a considerable quantity for any one site and, in toto, may contain a wide range of organic and inorganic contaminants. Historically, such acids have been treated by neutralisation but, as this practice becomes questionable, a recovery process must be identified which is capable of handling waste acids which may contain varying quantities of organic and inorganic impurities. Furthermore, the resulting product acid must be able to be recycled to any of the source processes.

Preliminary bench scale experiments have indicated that the organic contaminants in such acids are relatively easily oxidised. Therefore, in view of the extensive experience already gained with inorganic contaminated acids there is little doubt that the Chemetics' vapour phase technology can be applied to acids contaminated with both organic and inorganic components.

Developing Technology

The traditional atmospheric pressure, liquid phase concentration process (Pauling Process) has the advantage of operating above 300°C which in many cases with the addition of a suitable oxidising agent would allow for the oxidation of many organic contaminants in waste acids. However, the process is based on silicon iron equipment and consequently suffered from heat transfer limitations, high maintenance costs, corrosion and the possibility of catastrophic failure.

If these limitations can be overcome there are many attractions to an atmospheric liquid phase concentration process. Operation at atmospheric pressure results in much smaller equipment than for a vacuum concentration plant of the same capacity. It also, by definition, operates at temperatures at which organic destruction is readily achieved.

To this end Chemetics are actively pursuing the use of $SARAMET^R$ as a potential material for atmospheric concentration duties. SARAMET is a fully austenitic alloy with the nominal composition shown in Table 1.

TABLE I

ELEMENT	WEIGHT %		
Chromium	17.5		
Nickel	17.5		
Silicon	5.3		
Carbon	0.01		
Iron and other	remainder		
alloying Elements			



A paper on the use of SARAMET in sulphuric acid plants was presented at Sulphur 1882.

It is known that anodically protected SARAMET has excellent resistance to strong sulphuric acid (greater than 90% strength) up to the boiling point. In addition, SARAMET is an austenitic stainless steel and does not suffer from the heat transfer limitations of silicon iron. SARAMET is therefore an excellent material of construction on which to base atmospheric pressure, liquid phase concentration technology.

Chemetics have just completed experiments on one small pilot plant (see Figure 5) which was a batch SARAMET vessel designed for materials testing purposes. A smaller unit, designed to test various means of heat input, has recently commenced operations.

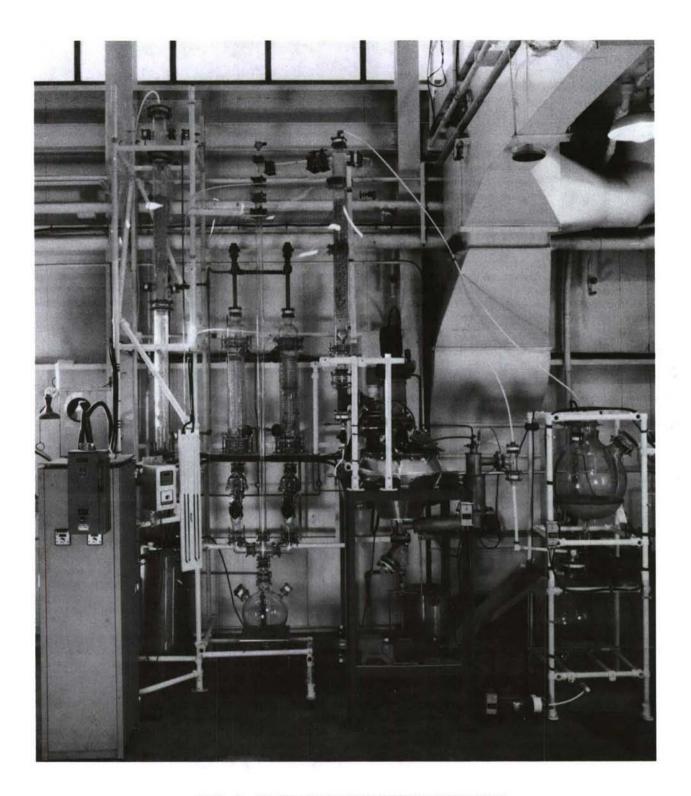


FIG. 5: SARAMET ACID CONCENTRATOR



Summary

Chemetics' objective is to develop technology such that all spent acids in both large and small quantities (I - 1000 TPD) can be treated and concentrated for recycle. This is gaining in importance as increasingly stringent legislation is preventing the utilisation of many traditional methods of acid disposal.

Examples are given of ways in which existing technology can be adapted to solve waste acid problems either by retrofits or by combination with a traditional technology.

Chemetics' new generation vapour phase technology and its possible application to a range of acids is discussed and, finally, the possible future application of SARAMET to the atmospheric pressure, liquid phase concentration of waste acid is described.

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COST PERFORMANCE ASSESSMENT OF IN SITU VITRIFICATION¹

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Steven R. Booth*

Abstract

In situ vitrification (ISV) is a thermal treatment technology with promise for the destruction or immobilization of hazardous materials in contaminated soils. It has developed over the past decade to a level of maturity where meaningful cost effectiveness studies may be performed. The ISV process melts 4 to 25 m² of undisturbed soil to a maximum depth of 6 m into an obsidian-like glass waste form by applying electric current (3750 kW) between symmetrically spaced electrodes. Temperatures of approximately 2000°C drive off and destroy complex organics which are captured in an off-gas treatment system, while radio-nuclides are incorporated into the homogeneous glass monolith. A comparative life-cycle cost evaluation between mobile rotary kiln incineration and ISV was performed to quantitatively identify appropriate performance regimes and components of cost which are sensitive to the implementation of each technology. Predictions of melt times and power consumption were obtained from an ISV performance model over ranges of several parameters including electrode spacing, soil moisture, melt depth, electrical resistivity, and soil density. These data were coupled with manpower requirements, capitalization costs, and a melt placement optimization routine to allow interpolation over a wide variety of site characteristics. For the purpose of this study, a single site scenario representative of a mixed waste evaporation pond was constructed. Preliminary comparisons between ISV and incineration show that while operating costs are comparable, ISV avoids secondary treatment and monitored storage of radioactive waste that would be required following conventional incineration. It is the long term storage of incinerated material that is the most expensive component.

INTRODUCTION

In situ vitrification (ISV) is a patented innovative environmental technology for remediation of sites contaminated with a variety of hazardous substances. It has been developed at Pacific Northwest Laboratory (PNL), beginning in 1980. The process is based on the joule-heating principle utilized in electric melter technology as developed at PNL for the immobilization of high level nuclear wastes. The



¹LAUR 92-2071

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Department of Energy granted the patent rights to Battelle, which created GeoSafe, Inc. to commercialize the technology in 1988. [1] The first full scale demonstration of ISV at an actual site was in June of 1987 at Hanford [2].

The purpose of this study is to evaluate the cost effectiveness of the ISV system in a specific site scenario. The goal is to investigate potential cost savings of this technology over a more conventional method. Since ISV does not replace one particular technology in all types of environmental clean-up, a remediation scenario is developed to put ISV and a chosen conventional remediation technology on an even basis in terms of treatment and long term immobilization of the waste.

COMPARISON METHODOLOGY

New environmental technologies are evaluated in terms of both performance and economics. The new technology is compared and contrasted with a baseline or more conventional technology. The first problem is how to make a comparison of two technologies that are not interchangeable. The method chosen is to construct a reasonable basis for comparison. These proposed comparisons are known as "performance scenarios" as detailed in previous studies [9,4]. Subsequently, the general performance scenario is considered in the context of several realistic waste sites. Each specific case is referred to as a "scenario."

Particular emphasis is given to the performance evaluation. Performance issues are critical for establishing a balanced comparison from which meaningful cost analyses can be obtained. The performance scenario equates the final treatment result of the competing technologies, so that cost effectiveness evaluation reduces to a direct comparison of costs. This approach eliminates the need for assigning qualitative weights to different outcomes. This method also allows one to ignore comparable components of cost that are subject to uncertainties, thus, emphasizing the cost differences between the technologies while providing a structured assessment of all stages of the technology life-cycle.

It is important to understand that in many cases the new environmental technology does not replace a current technology on a one for one basis. A new technology may replace or improve a portion of an existing technology, or it may replace a combination of conventional treatments. ISV may potentially replace several very different technologies. Thus, it may be necessary to look at a range of baseline technologies to fully characterize the role of the new technology in a remediation system. The major components of the methodology are:

- "Identify major performance characteristics of the new environmental technology."
- "Identify appropriate conventional technologies to serve as the baseline for performance comparisons."
- "Compare performance between the new technology and the conventional alternatives."

¹The Comparison Methodology section was developed in "A Standard Methodology for Cost Effectiveness Analysis of New Environmental Technologies" and "Cost Effectiveness of the Site Characterization and Analysis Penetrometer System (SCAPS)," listed in the references.

- "Use scenarios to provide a realistic context to the performance comparison."
- "Perform an economic comparison of the new technology and the conventional alternatives." Use the scenarios constructed above for a detailed cost savings analysis on a comparative life cycle basis.
- Assess uncertainty in performance, cost and regulatory restrictions to implementation.
- "Consider all other relevant aspects and/or effects involved in the use of the new environmental technology." When it is not possible to quantify these influences in scenarios due to lack of detailed information, provide a qualitative discussion. "Important issues to consider are: future developments expected in both the new technology and the conventional alternatives, applicability of the technology to different sites, health and environmental risk reduction, and regulatory status and perceived public acceptance."

IN SITU VITRIFICATION

In situ vitrification is applicable to hazardous inorganic and organic, radioactive, and mixed wastes. The desirable characteristics of ISV are the durability of the end product, permanent destruction of the organic components and reduced handling and exposure to the contaminated soil. The radioactive and inorganic components are thoroughly mixed throughout the melting zone, and there may be significant reduction of volume through elimination of voids. If the vitrification is done in situ, little or no excavation or transportation of the hazardous materials is required.

ISV process equipment specifications have been taken from an actual bid by the vendor for remediation of a Department of Energy site. The costs for equipment have been verified independently, and wage rates were adjusted to reflect national averages. The bid was based on the owner providing electric power, this estimate includes the costs for generating power on site. All costs have been adjusted to June 1992.

Process Description

The ISV system typically consists of a square array of four electrodes placed at the surface of the contaminated volume. A conductive starter path is established between the electrodes and an electric current is applied, introducing a large amount of energy into the low energy soil system and generating enough heat to melt the soil. As currently practiced, the electrodes are pushed into the soil as the melt proceeds.

In addition to the basic electrodes, the system includes a hood that covers the melt area. The hood provides a combustion chamber for the pyrolyzed organics and it supports the electrodes. This hood also collects the gases emitted during the decomposition, vaporization and combustion of various products in the soil. The gases are sent through appropriate processes that remove the hazardous components. The by-products of the off-gas treatment can be incorporated into a later melt to reduce the amount of waste to be ultimately disposed [3].

The off-gas treatment system consists of several stages. The gases are scrubbed with a quencher and a tandem nozzle scrubber, which remove particles down through sub-micron sizes. Then, the water aerosols are removed by a vane separator, followed by a condenser and a second vane separator. The gases are then heated to a temperature well above the dew point. Finally, the off-gas is filtered through two stages of High Efficiency Particulate Air (HEPA) filters [2].

ISV is designed for the purpose of thermochemically treating contaminants present in soil, without excavating the soil. However, it can also be applied to sludge, sediments, tailings or other types of wastes. Materials to be treated may either be vitrified in place or in some cases they may be excavated and moved to the treatment site.

The ISV system can process 800 to 1000 tons of contaminated soil in a single setting, at a rate of about 4 to 6 tons per hour [3]. The practical surface area treated in a single setting is up to 7.5 meters square, with multiple overlapping settings used to treat large contaminated sites. The maximum depth is about 6 meters, but the depth and surface area dimensions are subject to electrical design constraints which require that the electrodes be placed closer together as the depth of treatment increases.

Process Requirements

The ISV process requires that glass forming materials (e.g., Si and Al oxides) are present in sufficient quantities to form and support a high temperature melt [3]. Additionally, monovalent cations are required to provide sufficient conductivity for the process to efficiently operate. This requirement can be met by adding fluxing materials. Eighteen soil types from the US and Canada have been tested, including soils from the sites where ISV is most likely to be applied for environmental remediation. Most of the soils tested were capable of supporting a melt and producing excellent residual product without modification to the soil [3].

ISV is applicable to fully saturated soils. The water is first removed by vaporization, after which the process melts the dry materials. The energy required to remove 1 pound of water is about the same as the energy required to melt 1 pound of soil, so it is best to keep the material as dry as possible prior to treatment [3]. If the soil is below the water table, it may still be treated in situ provided that the recharge rate is slow enough. Alternately, the water table may be lowered below the treatment volume by conventional dewatering means, or the material to be treated may be removed from below the water table for processing.

Power requirements are not a limiting factor. Power for the ISV process is available from local utilities throughout the 48 contiguous states. The process requires 3 phase electric power at either 12,500 or 13,800 volts. The equipment draws about 3,750 kW during operation and consumes about 0.4 to 0.5 kwh per pound of soil [3]. This amount of power is not significant compared to the amount of power available from most US public utilities [3]. Process power may also be generated on site by diesel generator. Power interruptions are acceptable, and power outages of up to several days can be tolerated, as long as a molten path between the electrodes is maintained [3].



The ISV process equipment is on three trailers which must be placed on a level area, within 6 feet above or below the level of the treatment area. The off-gas containment hood has a flexible skirt that can accommodate +6 to -6 inch variations in soil surface, however the area supporting the hood should not slope more than 5% [3].

Structures above or below the ground immediately adjacent to the contaminated site should be evaluated for the effects of soil subsidence as well as thermal effects. The 100° C isotherm can move out to 5 to 7 feet beyond the melting zone. For initial estimation, the ISV melt should not be closer than 15 feet from utilities or structures that could be damaged by 100° C heat [3].

Final Waste Form

Tests on the end product from pilot scale field tests indicate several desirable traits for the treatment of hazardous materials. Organic compounds and some inorganic materials are destroyed or removed from the treated volume. The remaining hazardous components are incorporated and immobilized into a stable mass. The vitrified soil remains virtually without cracks, and upon intentional fracture reveals a nonporous glass similar to a naturally occurring volcanic glass known as obsidian [3]. ISV eliminates the voids, water and volatile components found in a waste site, resulting in significant volume reduction [3]. The product exhibits conchoidal fracturing, which is self terminating The fracture mechanism and the nonporous nature of the vitrified soil make it resistant to freeze-thaw cycling [5].

Leach tests on the vitrified blocks show leach rates significantly less than marble or bottle glass, and comparable to Pyrex or granite. Projected leach rates are three orders of magnitude below the current detection limits. The ISV waste form is expected to remain unweathered for much greater than 10,000 years [2] The final waste form has been demonstrated as capable of passing the EPA's EP-Tox, SWLP, and TCLP leach tests [3]. Test results indicate that it may be possible to delist vitrified wastes [3].

Vitrification of radioactive wastes results in some attenuation of radiation by the mass of the treated block. Additionally, the final waste form is difficult to violate by accident due to its strength and continuity [3]. ISV incorporates the source of radon gas, radium-226, in the end product. When the radium-226 decays into radon, the radon is held in the glass until it decays back into a solid state. The radon emanation rate is reduced by four orders of magnitude [3].

INCINERATION

Incineration is one of the most widely used and best understood technologies for treating organic wastes. Research by the EPA has shown that properly designed and operated incinerators have negligible health risks or environmental impact [8]. Because incineration is widely used, and the final waste form is acceptable, it is the baseline technology chosen for this report.

Incineration works by oxidizing the wastes. Wastes are first excavated and transported to the incineration site. The wastes must be preprocessed to break up or remove large inclusions. The incinerator can be either a very large capacity plant, or a smaller mobile unit that is moved to the site.

Incineration is most applicable to organic waste. It can also be used on mixed inorganic and organic wastes, by first incinerating to remove the organic component, then chemically stabilizing the inorganically contaminated remainder. Mixed waste including radioactive components can also be processed by incineration. After incineration, the final waste form must be disposed of properly.

A transportable incineration system has been configured to facilitate identifying the components, sizing the major equipment items, and forming the basis for a comparative cost estimate. This system is intended to be assembled at the DOE Hanford Reservation, used exclusively for cleanup of contaminated sites at that location, and eventually disposed of on that site. Process equipment items are to be assembled in several transportable units designed so as to facilitate unit integration through the use of jumper connections. Siting of the system is such that waste excavated contaminated soil and other solid waste may be fed directly into the treatment facility without transporting by truck. The system has been specifically designed for the purpose of comparing a transportable system for incineration of solid mixed waste with in-situ vitrification.

The study assumes that no TRU or high level waste is to be processed and that none is produced by the volume reduction associated with the waste treatment. The system is designed to accommodate either drum filling of treated waste product by remote control or temporary storage for later use in site close out and restoration. The entire process, except for the final reheating and filtering of product gases, operates at below atmospheric pressure to prevent escape of air pollutants.

Process Description

Contaminated soil or other waste is excavated by bucket excavator or other suitable device and loaded onto a moveable conveyor. The conveyor feeds a shredder / delumper where it is reduced in size to three inches or less. From the shredder / delumper the waste is fed to a hammer mill where it is further reduced in size to one inch or less. Sized feed from the hammer mill is conveyed by screw conveyor to the system feed bin. The process is fed from the feed bin at a rate of up to nine tons per hour of waste containing five percent moisture via a weigh belt conveyor. The weighed waste is fed into a rotary kiln incinerator where it is heated by combustion gases produced by burning fuel oil in air. Solids leave the incinerator at a temperature of 1400° F. The combustion gases leave the incinerator at a temperature of 1600°.

Hot solids from the incinerator are mixed with recycled cooled product and conveyed to the clean solids collection bin by a water cooled screw conveyor. Further cooling is accomplished by water sprays in the solids collection bin. From the solids collection bin the product is partially recycled with the net product going to product storage. Product storage is by placing either in 55 gallon drums or in a temporary storage pile. Product going to temporary storage is further dampened with water for dust suppression.

Combustion gases form the incinerator are passed through a secondary combustion chamber where additional fuel oil is burned to raise the temperature to 2200° F. Residence time in the secondary combustor is a minimum of 2 seconds. The capability to reach this temperature level is provided for the event of PCB's or

other chlorinated solvents being present in the waste feed. Temperatures could be reduced to 1800° F if no PCB's or chlorinated solvents are present in the waste. Gases exiting the secondary combustion chamber are cooled to 400° by water injection. The product gases are further cooled to 300° by heat exchange with a heat transfer fluid operating between 200° and 350°. The gases are finally cooled to below 200° by water spray injection. The cooled gases are then water scrubbed in a venturi scrubber with an alkaline solution for removal of sulfur dioxide.

The cooled and scrubbed gases are fed through a blower through heat exchange with the hot heat transfer fluid where they are heated to 267°. Finally, the reheated product gases are filtered through a bag filter followed by HEPA filters and discharged through a stack to the atmosphere. Water from the venturi scrubber discharge is cooled with an air cooler and recirculated. A side stream of the recirculated water is withdrawn and treated by clarification. Sludge from the clarification process is drummed for disposal.

SCENARIO

Site Characteristics

The site where the two technologies will be applied is critical to the analysis. Changes in the type of waste or other factors will affect the cost of both processes. For the purposes of this investigation, a specific site scenario has been developed. This site is similar to mixed waste trenches and pits that are found on DOE property.

The site in our study is 30 meters wide by 90 meters long by 5 meters deep. The soil is homogeneous, and contaminated with low level radioactive mixed waste. The soil moisture content is 5%. The entire contaminated site is located within a larger government owned facility.

Basic Assumptions

In order to compare a new and innovative technology to a baseline standard technology, certain assumptions have been made. The first is that the baseline technology has been in operation long enough to have the start up problems solved, and the second is that the process equipment and materials are suitable for the application.

The use of a mobile rotary kiln incinerator was predicated on the comparability to the ISV method, which is in itself a mobile remediation method. Other options included slagging kiln incinerators, multiple hearth roasters, and fluid bed dryers, but were not considered suitable in this instance. The mobile incinerator was chosen due to it's flexibility and low capital cost, combined with the minimal D&D cost at the end of it's useful life.

There are many issues that have not been addressed here in terms of true life cycle costs. Our goal has been to concentrate primarily on the differences in cost between the two technologies, also known as cost deltas. Several real costs have

been left out of the analysis, but only after deciding that they would be similar between the two processes.

In comparing the incinerator option to the ISV, the following qualitative discussions have been advanced in order to remove some of the lesser known factors influencing the choice of technology.

ISV is taken to be an established technology, and not subject to any special permitting or monitoring requirements. This may not prove to be the case, but for the purposes of this report this assumption is necessary to make an accurate comparison. ISV is also given the benefit of the results of the leach tests, and the glass monolith created by the ISV process is left in place with only minimal monitoring wells placed.

In both cases, the Remedial Action Plan (RAP) will need to be approved prior to commencing operations. The main point of discussion hinges on the difference between a known incinerator technology, with high gas flows and a potential for particulate release, versus a new and untried technology that has only a low gas release from the evaporation of the organics. Therefore a cost difference between the two cases has not been considered, although it is recognized that licensing and permitting may certainly add a considerable cost to the overall project life cycle.

The chosen site will most certainly need to be characterized prior to the preparation of a Remedial Action Plan, and in most cases would consist of drilling and sampling of the contaminated area. Given the accuracy of this study, we have decided to exclude the cost for initial site characterization due to the relatively low cost delta.

In both cases under consideration, there will need to be some form of long term monitoring and surveillance of the remediated site and the secondary wastes, unless the regulatory agencies determine that the final obsidian like form of the vitrified mass is inert enough to classify beyond the 10,000 year limit. In the absence of this ruling, we have decided to consider that long term maintenance and surveillance will be performed by a series of monitor wells around the perimeter of the remediated area, and that the cost of maintenance and surveillance of the incinerated and stored product in included in the cost quoted in our economic analysis.

Due to the fact that all of the sites under consideration are owned by the DOE, and that it is unlikely for them to release any of these sites to the general public, the concerns of returning the land back to grassy playing fields does not enter the equation. In most cases, the land would be remediated and left in a vacant form for possible future DOE use. We have therefore excluded any costs for turning the land over to public use.

It will be necessary to develop a site specific ES&H plan for the project before any remediation can take place. It is anticipated however that the cost for an ES&H plan for either case will be approximately the same.

Since the scenario site is within government property, it is assumed that the remediation contractor will not need to be responsible for ensuring that only approved personnel are allowed access to the project site. There will be a fence around the remedial action site, solely for protection against theft and tampering.



As the site will be operated 24 hours/day, it is considered to be secure at all times.

The project costs have been brought forward to June of 1992 for both technologies and forward escalation for operating personnel and consumable items are included in the case studies.

Detailed Cost Basis

The following items are representative of the costs that are included in the estimates for ISV and incineration. Unless otherwise noted, each of the categories have been included in both estimates.

Site Preparation and Temporary Facilities

The site is considered to be in a flat and readily accessible area, and will require only minimum clearing and leveling prior to remediation. The perimeter fencing will be 10 ft high with 4 strand razor wire topping.

Shower and toilet trailer, change room, lunch trailer, storage trailer, communications system, and site vehicles have all been included as temporary facilities. Power (generator), water (stored) and telephone are included as temporary utilities.

Process Equipment

Engineering design and procurement has been included at 15% of the total installed equipment cost, and includes the initial bench test and checkout for both processes.

Detailed estimates for both processes have been performed. For the incinerator the majority of the material handling system has been priced from Richardson Estimating Systems manuals for industrial process equipment, and factored to include the necessary dust suppression and collection system. The bucket wheel excavator was quoted as a budget price by Man GHH Corp., (Pittsburgh) and the rotary kiln was quoted from historical data supplied by Kennedy Van Saun Inc. (Pittsburgh), and includes the feed hopper, drag conveyor, incinerator and drives, secondary combustor, scrubber, baghouse and instrumentation mounted on a legal over-the-road trailer. The off-gas collection and treatment system was priced from either Richardson Estimating Systems, or quoted as budget prices from TAG Inc. (Englewood, Colorado).

Ducting, piping, electrical interconnections and instrumentation were factored from the base equipment cost, using industrial factors for incineration facilities as listed by the American Association of Cost Engineers. (Cost Engineers Handbook)

The ISV system costs came originally from a detailed estimate by the vendor for a remediation project for the Department of Energy. These prices have been verified where possible, and have been modified to reflect the scenario developed for this study.

Both estimates include an annualized fixed rate charge of 20% calculated from a useful equipment life of 10 years (10%/year), plus a 7% cost of money, plus an

allowance of 3% for taxes and revenue. The cost of selective equipment replacement during the 10 year life cycle has been included in the contingency factor of 15%.

Routine maintenance of both systems has been included based on a percentage of the operating time.

Mobilization and Demobilization

Both estimates include allowances for mobilization to the site and erection of process equipment, as well as dismantling the plant and performing necessary decontamination when the project is finished.

Project Management & Administration

To cover the cost of project management, site administration and home office overhead, a factor of 8% was applied to the total cost of the physical facility.

Operating Cost

The operating costs are based on a 180 day cycle for incineration and a 250 day cycle for ISV, and are industry averaged. This category includes the cost of all consumable items, stack sampling and sample analysis. Although there is no cost delta involved, a full time radiation monitoring health physicist will be employed at the site and charged to the project operating cost in both cases.

Incinerator Operation

Based on the 13,500 m³ to be remediated, and using the rated throughput of 8 ton/hr it was calculated that 180 days would be required to complete the site clean up. It was decided that a 4 shift operation would allow 1 hour each shift for maintenance, and allow the overlap of personnel at shift end. Travel and living costs were included for 12 personnel, and the balance of the operating crew were considered to be local hire.

ISV Operation

Based on a model developed by GeoSafe, the ISV operation will require about 72 hours per setting, and 70 settings to complete the site. Operating 24 hr/day and allowing for maintenance and downtime between settings it will require about 250 days to complete the vitrification portion of the project. The cost of moving the operating staff to the site is included in the analysis. In addition to the ISV equipment operators who are moved to the site, local skilled labor will be hired for setting up the equipment and moving between settings.

· Equipment Maintenance

The labor costs for maintenance have been calculated based on a percentage of operating hours and the travel and living costs have been included in the operating labor cost.



Disposal Cost

The incinerator option can be used with either mixed waste, low level waste or radioactive mixed waste. In this case, the scenario is for the radioactive mixed waste, at a 5% to 10% moisture content, which requires us to consider the equipment to be contaminated from the start up. We have therefore assumed that all of the resultant waste will need to be contained in 55 gal Low Specific Activity (LSA) drums, and transported to a licensed waste depository. The costs for the 55 gal LSA drums, the transportation costs and the storage costs were taken from the Rocky Flats Plutonium Recovery Modification Project (PRMP) of March 1989 and modified to reflect current prices and practices. It is important to recall the earlier assumption that no TRU wastes are present in the contaminated site, nor will any be produced by volume reduction. The cost of secondary waste disposal is significant, representing the largest component of the total cost. It is therefore important to note that these costs are subject to revision in the final report of this project to the DOE.

ISV will generate a small amount of material in the off-gas processing that will have to be ultimately disposed of. The cost of this disposal is based on the same unit costs as were used for disposal of the incineration wastes. The vitrified mass generated by ISV will be left in place.

D&D Cost

Based on the Rocky Flats PRMP study, the cost of D&D was annualized over the life of the project. In both instances, the process equipment is disposed of at the end of its 10 year useful life.

Backfill and Grade

The hole created by the excavation for incineration will be filled, compacted and graded. The ISV process will cause subsidence of the soil. The vitrified material will be covered with backfill and brought back to grade.

Environmental Impairment Insurance

Using a quotation from Alexander & Alexander for the GeoSafe ISV estimate, we have assumed that the insurance is based at \$0.023 per \$1,000 of coverage, with an addition \$40,000 for Comprehensive General Liability insurance. Both estimates include \$10 million of environmental impairment coverage, for a total insurance cost of \$270 thousand.

Escalation

Both projects have been escalated based on the two-thirds completion point. Cost of fixed equipment is excluded from the escalation as it is purchased at the beginning of the project, and the cost of financing it has already been covered elsewhere.

Contingency

Due to the uncertainties involved with the project scope and level of definition, it was decided that a contingency of 15% was applicable in this instance. This value would include errors and omissions within the scope of work and allowances



for minor equipment replacement. Any changes to the project scope would require that the project be increased/decreased accordingly.

RESULTS

Based on the scenario that was developed, ISV is significantly less expensive than incineration. ISV was found to cost \$680 per cubic meter, versus \$2015 per cubic meter for incineration. Figure 1 below shows the comparison of the major cost categories, excluding secondary waste disposal. The column for secondary waste disposal for incineration would be over four times the height of the next tallest bar.

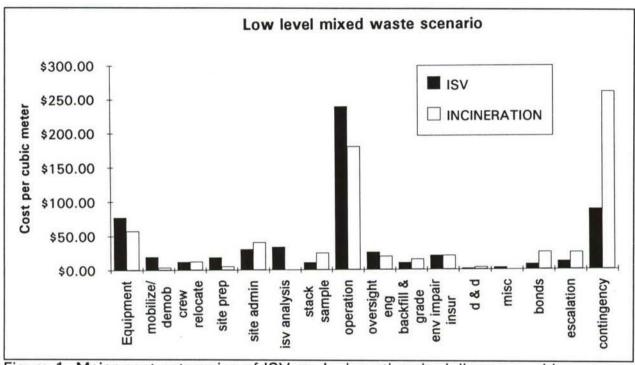


Figure 1. Major cost categories of ISV vs. Incineration, in dollars per cubic meter.

Examination of specific cost categories listed in Table 1 on the next page highlights the differences in cost.

Capital equipment costs are similar for the two technologies. ISV costs slightly more due to the decision to generate power on site. Purchasing power from a local utility would eliminate the need to purchase a generator.

Mobilization of the ISV system is much more labor intensive than it is for incineration in the scenario developed here. In the final report, the mobilization will be optimized to better reflect the realities of construction.

The ISV system includes extensive sampling of the vitrified area to verify that the final waste form is acceptable. This adds over 450 thousand dollars to the total cost of ISV. Both estimates include extensive stack sampling and analysis. Incineration incurs over twice the cost of ISV in this category due to much larger air flow through the incinerator.



Although incineration operates for a shorter time, it has a higher labor cost during operation. One reason for this is the increased worker protection requirements for incineration over ISV. The protection reduces the efficiency of the labor force.

Cost category	ISV: total scenario cost	ISV: cost per cubic meter	Incineration- total scenario cost	Incineration: cost per cubic meter	difference: Incineration - ISV
Equipment	\$1,038,654	\$76.94	\$775,557	\$57.45	(\$19.49)
Mobilize/ demobilize	\$261,820	\$19.39	\$48,584	\$3.60	(\$15.80)
Crew relocation	\$160,000	\$11.85	\$161,820	\$11.99	\$0.13
Site preparation	\$247,310	\$18.32	\$72,468	\$5.37	(\$12.95)
Site administration	\$403,183	\$29.87	\$544,731	\$40.35	\$10.49
ISV melt analysis	\$452,939	\$33.55	\$0		(\$33.55)
Stack sampling	\$140,321	\$10.39	\$328,000	\$24.30	\$13.90
Operation: labor	\$1,010,902	\$74.88			
Operation: consumables	\$2,057,316	\$152.39	\$1,328,400	\$98.40	(\$53.99)
Operation: subcontracts	\$140,291	\$10.39		K-Sharan	(\$10.39)
Oversight engineer	\$345,600	\$25.60	\$259,200	\$19.20	(\$6.40)
Backfill & grade	\$135,628	\$10.05	\$202,500	\$15.00	\$4.95
Secondary waste disposal	\$1,038,310	\$76.91	\$17,877,816	\$1,324.28	\$1,247.37
Environmental impairment insurance	\$270,000	\$20.00	\$270,000	\$20.00	\$0.00
Decommission & dispose	\$20,822	\$1.54	\$44,109	\$3.27	\$1.72
Miscellaneous	\$37,468	CV-XCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC		\$0.00	(\$2.78)
Labor & material, & performance bonds	\$100,954	\$7.48	\$345,218		\$18.09
Escalation	\$156,147	\$11.57	\$336,367	\$24.92	\$13.35
Contingency	\$1,186,405	\$87.88			\$171.57
Total	\$9,212,070	\$682.38	\$27,198,732	\$2,014.72	\$1,332.35

Table 1. Cost comparison of ISV and Incineration for a 30m x 90m x 5m deep mixed waste site.

ISV is more expensive in the consumables category. The electrodes are expensive and they are consumed during the melt. The power requirements for ISV are high, and since our scenario includes generating power on-site, there is a large cost for diesel fuel included in the consumables line item.

The cost of secondary disposal is the most expensive component of the cost of incineration. ISV creates a vitrified mass that may be left in place, while incineration requires that the residual be moved to monitored storage.

In the case of a scenario where secondary disposal is eliminated, the total cost of incineration will be similar to the total cost of ISV. If there were only a hazardous organic component to be destroyed, there would be little or no waste to be disposed of under incineration, and the contingency could be reduced significantly. Allowing a minimal cost for secondary waste in each case, and reducing the contingency accordingly, results in incineration being around \$500 per cubic meter, slightly less than ISV which costs about \$600 per cubic meter.

Other Considerations

Differences in Final Waste Form

The final waste form of ISV can not be compared easily with the final waste form of incineration. The ISV glass monolith is left in place, and the incineration product must be packaged and put into long term storage. Ultimate use of a site that has been vitrified versus a site that has been cleaned up by incineration or other technologies will have to be considered. Regulations restricting use of a site will affect the selection of a remediation technology in a way that is not possible to consider in a general life cycle cost analysis.

FUTURE DEVELOPMENTS

Now that a general model has been constructed, other scenarios can be run. It will be possible to quickly perform a comparison between ISV and incineration under other specific site conditions.

The full report of the findings of this study is forthcoming. It will provide more detail regarding the process equipment, required labor force, and other aspects of the operation. Additional discussion will include the performance study of ISV will be included. Performance of ISV was investigated under conditions of varying soil moisture, site geometry, glass density, electrical resistance and other factors Readers needing more detail are referred to the final report.

Finally, the reader is cautioned that sensitivities have been identified and are under ongoing review. The findings of the final report will reflect any new information that is discovered.

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SUPERCRITICAL CO₂ CLEANING FOR WASTE MINIMIZATION^a

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Introduction

Production facilities in the US Department of Energy complex employ a variety of solvent-based cleaning methods for removing residues that might alter the manufacturing process, corrosion chemistry or function of weapons components. Many of the solvents are hazardous chemicals such as volatile organic compounds. Some are chlorocarbons and chlorofluorocarbons that are environmentally unacceptable, generate hazardous waste and are subject to existing or impending regulation. Supercritical CO₂ is a moderately good solvent for organic compounds. It also appears to satisfy environmental criteria not met by chlorofluorocarbon solvents in use. Supercritical conditions are attained at modest conditions (above 31°C and 1087 psi). The high volatility of CO₂ facilitates solute separation and the likelihood of solvent recycle. CO₂ is economical, naturally occurring, non toxic, unreactive and poses minimal ES&H risk. Supercritical CO₂ technology is well developed and widely used for extracting organic compounds in food, polymer, pharmaceutical and synfuel industries. Large-scale supercritical fluid systems are commercially available for extraction, but only recently have several US companies begun to design and build units for cleaning.

The objective of this supercritical fluid CO₂ program at Los Alamos National Laboratory is to develop supercritical fluid carbon dioxide as a recyclable, non hazardous solvent for cleaning some weapons components. Prior studies at DOE's Rocky Flats Plant¹ show that organic residues on steel and uranium surfaces cleaned with supercritical CO₂ and with 111-trichloroethane are comparable. Recent vendor tests show that large steel objects can be cleaned at easily accessible temperatures, pressures, flow rates and times to levels that are a hundred-fold cleaner than that required for plutonium weapons components. A description of the technology, some of our data, and our planned scale-up activities are presented herein.

Cleaning Concept

The concept of using a condensable gas for cleaning is simple. As the diagram at the right illustrates, the gas is first pressurized and then circulated through a pressure chamber containing the articles to be

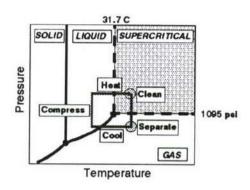
cleaned. The fluid that removes the contaminants from the articles is then replaced with clean fluid. The dirty fluid passes into a separator where the pressure is reduced. The cleaning fluid returns to gas and the less volatile contaminants collect at the bottom of the separator for collection. The gas phase proceeds to a refrigerated condenser where it is liquified and ready for recirculation. In the case of carbon dioxide, liquification can be accomplished at modest pressures and ambient conditions. Its nonflammable nature makes it especially attractive.

PUMP VENT REFRIGERATOR

a Program funded by Department of Energy.

Since liquid carbon dioxide is generally not thought to be a particularly good solvent, improved extraction capability is usually sought by taking the liquid to its supercritical state. This can be achieved with carbon

dioxide at temperatures slightly above ambient (see figure at right). Utilizing supercritical carbon dioxide, the cleaning scheme would involve performing the cleaning in the supercritical region, dropping the pressure into the gas region to effect the separation, then cooling the gas to condense it, and then compressing and heating the liquid back up to the supercritical state. The size of the Carnot cycle described, of course, will influence the cost of the operation. The higher the pressure the process must be run at, the more expensive the capital outlay must be. To help equipment designers, researchers need to determine the smallest cycle that will produce acceptable results in a large number of cleaning cases. The rhetorical question

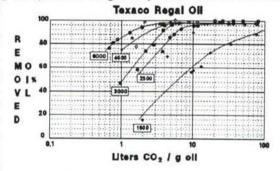


"How clean is clean?" is more relevant to "How clean do you need it?" than it is to the absolute level of cleanliness. Researchers at several DOE laboratories are looking at this issue.

Some Experimental Results

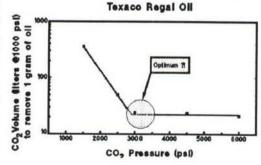
To evaluate the cleaning of oil from aluminum surfaces, we have used an ISCO supercritical carbon dioxide extractor. For the data presented here, the temperature was held constant at 40°C and the pressure was varied from 1500 to 6000 psi. A light-weight machining oil (Texaco Regal Oil) was chosen as the

contaminant. A small amount of oil (approximately 5 mg) was placed on an aluminum pan with a surface area of 1 cm². The pan was placed in the 10-ml extractor which was then filled with carbon dioxide to the desired pressure. After remaining in contact with the pan for 10 minutes, the carbon dioxide was released, the amount of oil removed was determined, and the procedure repeated. Results are presented at the right. Within the temperature-pressure space studied, the pressure did not appear to control the level of oil removal achievable. The pressure did control the number of cleaning operations and, hence, the amount



of carbon dioxide needed to achieve the ultimate cleanliness level. This is more easily seen when the amount of fluid needed to remove 1 gram of the oil to the ultimate level is determined (see the figure at

right). In this particular case, pressures above 3000 psi are not justifiable, but pressures below this level require the pumping of large amounts of fluid to achieve cleaning. In a cleaning operation, recirculating the fluid at a lower pressure may be the most economical. In a once-through/discard-the-fluid process, knowing the minimum optimum fluid usage is an absolute must. The actual optimum pressure may be below the 3000 psi found in this case because the experiment was conducted in static mode and the efficiency was probably lower because the pressure was let down between incremental cleaning steps. In a



dynamic system, removal rate will also determine the cleaning efficiency. Indeed, the removal rate and not the solubility of the contaminant in the cleaning fluid is the issue in cleaning. Preliminary results suggest that this oil can be removed from the surface quickly (i.e., in less than a minute). Experimental data are indeed very encouraging for using carbon dioxide for cleaning, but the unwary should be cautious of what data are being presented. Much of the cleaning data to date is determined by watching the contaminant level in the fluid stream disappear. Thus the data indicate the rate of cleaning fluid dilution and



replacement. Fortunately, the actual removal rate is often faster than the reduction of contaminant in the cleaning fluid stream.

Scale-Up Activities

In addition to fundamental studies with bench-scale equipment, Los Alamos National Laboratory is working with industrial firms to make the technology more commercially relevant. DOE laboratories and industrial firms with cleaning problems and fluid handling experience are working together through a group called JAAST (The Joint Association for the Advancement of Supercritical Fluid Technologies). Through this group and a cooperative research and development agreement (CRADA), Los Alamos National Laboratory is working with Hughes Aircraft to determine the aspects that will allow the cleaning fluid to be recycled. For this activity, we have had Autoclave Engineers build a fully computerized, 16" diameter by 16" high cylindrical cleaning unit. It has a CO2 delivery capability of 500 pounds per hour at temperatures up to 60°C and pressures up to 5000 psi. The cleaning vessel is a 4' cubic module connected to the processing. separation, storage, refrigeration, and pumping modules. The latter modules occupy an area approximately 3' deep by 16' long and 9-1/2' high. The system is modular so that specially designed cleaning units can be utilized with the same processing system. The particular cleaning module we are getting is highly polished for high precision cleaning needed for computer, optics, and space electronics applications. As a consequence of this scale-up effort, firms interested in this technology will have a more convenient size to extrapolate from. Our work will thus have more commercial relevance than if we stayed exclusively with a bench-scale operation. Once the shakedown and recycle studies have been completed. we hope to be user friendly for friendly users.

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Aluminum Vapor Deposition As a Possible Replacement for Cadmium Electroplating

by

Robert Hoye and Robert Ressl IT Corporation

for

16th Annual Army Environmental R&D Symposium Williamsburg, Virginia

June 1992

PREFACE

This paper presents a summary of information contained in the USATHAMA report titled "Evaluation of Aluminum Ion Vapor Deposition as a Replacement for Cadmium Electroplating at Anniston Army Depot," Report No. CETHA-TS-CR-91054, April 1992. This report was prepared by IT Corporation under Contract No. DAAA15-88-D-0001.

INTRODUCTION

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) conducts research and development projects in support of the Army's goal to minimize the generation of hazardous wastes at Army depots. One such project involved demonstration testing of a full-scale Aluminum Ion Vapor Deposition System (AIVD) at the Anniston Army Depot (ANAD), Anniston, Alabama. The objective of this test was to evaluate the concept of replacing cadmium electroplating, which generates significant quantities of hazardous wastes, with aluminum ion vapor deposition, which generates almost no waste. Both cadmium electroplating and aluminum vapor deposition can be used on metal parts to provide a protective, corrosion-resistant finish. If the AIVD technology were to replace cadmium electroplating at ANAD, it would reduce or eliminate 1) employee exposure to cadmium and cyanides, 2) the expense of treating cadmium and cyanides in spent plating solutions and rinse waters, and 3) the expense and potential liability associated with the disposal of cadmium- and cyanide-containing hazardous wastes.

More than 70 AIVD units are currently in successful commercial operation. Most applications involve the plating of aircraft parts with a pure aluminum coating laid over an aluminum-alloy substrate to provide corrosion protection. In addition, this technology can be used to plate other metal substrates. The U.S. Navy uses AIVD at the Jackson-ville and Pensacola Naval Air Stations to coat aircraft parts. Parts used in marine environments are plated with aluminum for corrosion protection because such coatings last more than twice as long as cadmium coatings. Also, the AIVD system is reported to be more effective in coating corners and recessed areas than is cadmium electroplating.

Over the past 10 years, the AIVD technology also has been used successfully by other organizations. The U.S. Army has aluminum-coated depleted uranium; Westinghouse has coated powerplant steam turbine blades; Douglas Aircraft and United Airlines have used AIVD coatings on DC-10 aircraft; and McDonnell has used AIVD coatings on F-4, F-15E, F-18, and AV-88 aircraft. Additionally, Boeing, Pratt and Whitney, SPS Technologies, ACF Industries, and Hi Shear have successfully used AIVD coatings for parts in field service.

The aluminum ion vapor coating process is impacted by few regulatory restrictions while cadmium electroplating is extensively regulated because cadmium is both toxic and a potential carcinogen. Regulation of cadmium and cadmium wastes has a significant impact on the cost of cadmium electroplating. Additional regulations are anticipated and will result in higher costs. This will make alternatives such as AIVD more cost competitive.

This paper provides a summary of the information acquired during the AIVD demonstration project. Background information is presented along with a description of the AIVD process, a summary of cadmium and cyanide usage at ANAD, a discussion of applicable coating specifications, and torque requirements for plated fasteners. The results of the demonstration tests are also summarized.

BACKGROUND INFORMATION

AIVD Process Description

AIVD is a patented technology manufactured solely by Abar Ipsen Industries. The technology was originally developed by McDonnell-Douglas Corporation for use on aircraft parts. The AIVD operating principle is based on deposition of positively-charged aluminum ions onto a clean, negatively-charged, metal surface. After parts are placed in the unit, the chamber is evacuated to reduce the air pressure to a maximum of 9x10⁻⁵ Torr. Argon gas is then introduced to raise the pressure to about 6x10⁻³ Torr. A high-voltage discharge is used to ionize some of the argon to produce positive ions that bombard the negatively-charged metal surface and provide final cleaning. After the Argon cleaning, pure aluminum wire is fed into ceramic electrical-resistance heaters called "boats," where the wire is melted and vaporized. The boats move through the chamber to provide even distribution of the aluminum. Aluminum ions are attracted to the metal surface and deposited as a thin metal film. When aluminum parts are coated, nitrogen gas is introduced into the chamber during the operation to cool the aluminum parts and preserve their temper. Parts being plated are either placed in a metal mesh barrel and tumbled during the plating process (barrel coating) or suspended from a rack or other

support, depending on the size and configuration of the part being coated. After the coating is applied, the surface is subjected to a peening process to densify the coating.

Metal surfaces must be cleaned thoroughly before plating to achieve satisfactory adherence of the aluminum coating. All prior coatings, oil, and other organic matter must be removed from the surface of the part, and the metal surface must be prepared for plating by grit blasting. When handling parts prior to processing, operators must wear gloves to avoid contaminating the metal surfaces with body oils.

Cadmium and Cyanide in ANAD's Electroplating Facility

Cadmium electroplating operations generate the following Resource Conservation and Recovery Act (RCRA) listed hazardous wastes as defined in 40 CFR Part 261:

F006 - Wastewater treatment sludges from electroplating operations

F007 - Spent cyanide plating bath solutions from electroplating operations

F008 - Plating sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process

F009 - Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process

In 1990, ANAD reported that 14,700 pounds of hazardous waste was generated by cadmium electroplating operations (not including wastewater). Disposal costs were \$7,340 for hazardous waste disposal (\$0.50 per pound) and \$91,250 for wastewater treatment in ANAD's IWTP (\$0.365 per gallon) for a total waste disposal cost of \$98,590. More stringent regulatory standards would increase the cost of compliance or could render compliance unachievable with the current operational configuration and waste treatment/disposal system.

The following sources of information were used to estimate quantities of cadmium and cyanide involved in cadmium electroplating at ANAD.

- A description of the cadmium electroplating facility at ANAD compiled during several visits to the depot
- Estimated amounts of cadmium and cyanide in the system, and their annual consumption
- Reported quantities of hazardous waste generated from cadmium electroplating

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Amount of plating shop wastewater processed in ANAD's industrial wastewater treatment plant (IWTP)

Table 1 presents cadmium and cyanide usage data for ANAD in 1990. The data are based upon the estimated production rate and an average coating thickness of 0.5 mil (0.0005 inch).

TABLE 1. CADMIUM AND CYANIDE USAGE AT ANAD IN 1990

Parameter	Usage	
Capacity of plating lines	6,140 gal	
Concentration of cadmium	4 oz/gal of solution (typical)	
Concentration of cyanide	20 oz/gal of solution (typical)	
Cadmium/line	1,500 lb	
Cyanide/line	7,700 lb	
Additions of cadmium	2,500 lb	
Additions of cyanide	1,600 lb	
Cadmium to product	1,700 lb	
Cadmium to waste sludge and wastewater	800 1b	
Cyanide waste	1,500 lb	
Cyanide air losses	100 lb	
Wastewater	250,000 gal/yr	

Use of AIVD technology as a total replacement for cadmium plating could eliminate the rinse water stream (250,000 gallons per year) and the cadmium plating tank wastes. The stripping tanks would continue to be a source of cadmium waste, however, because cadmium-plated parts currently in field service would continue to be stripped prior to plating. If AIVD completely replaced cadmium electroplating, this waste source eventually would be eliminated.

Coating Specifications and Performance

Two specifications are applicable to the coatings evaluated: 1) Federal Specification QQ-P-416E, Amendment 1, February 27, 1987, for electroplated cadmium; and 2) Military Specification MIL-C-83488C, July 30, 1987, for vapor-deposited aluminum. Both specifications identify three classes of coatings based upon coating thickness. Table 2 presents minimum coating thickness requirements.

TABLE 2. SUMMARY OF MINIMUM COATING THICKNESS REQUIREMENTS FOR CADMIUM ELECTROPLATES AND VAPOR-DEPOSITED ALUMINUM (Coating thickness, mils)

	Cad		
Class	Area touched by 0.75-in. ball	Area not touched by 0.75-in. ball	Aluminum
1	0.50	0.30	1.00
2	0.30	0.20	0.50
3	0.20	0.15	0.30

The specifications require that corrosion protection be demonstrated by the coating's ability to withstand testing in a salt spray cabinet (Table 3). As indicated in the table, aluminum coatings provide substantially more protection. For example, Class 3 aluminum coatings provide more protection than Class 1 cadmium coating.

Both specifications require visual inspection of coated parts and destructive testing of steel test coupons that have been simultaneously plated with actual parts.

TABLE 3. CORROSION-RESISTANCE REQUIREMENTS OF CADMIUM
AND ALUMINUM COATINGS
(Hours in salt spray booth)

Ca		um	Aluminum	
Class	Without conver- sion coating ^a	With conver- sion coating	Without conver- sion coating	With conver- sion coating
1	96	168	504	672
2	96	168	336	504
3	96	168	167	336

Conversion coating is a chromate coating that provides additional protection and a good base for painting.

The specification for salt spray corrosion testing states that the appearance of white corrosion products on the aluminum coating during the test period is not cause for rejection. This direction differs from the specification for cadmium plating. White corrosion products may appear on AIVD coatings because aluminum is both a protective and a sacrificial coating. The aluminum corrosion product is aluminum oxide, a white material, and indicates that the aluminum coating has performed its function.

Table 4 presents a comparison of the performance of cadmium electroplates and AVID aluminum coatings under various conditions.

TABLE 4. COMPARISONS OF SERVICE LIMITATIONS
AND RESTRICTIONS FOR CADMIUM AND ALUMINUM COATINGS

Item	Cadmium electro- plates	AIVD aluminum coatings
Potential for hydrogen embrit- tlement of steel having a Rock- well C hardness of 40 or more	Requires 3 hours baking at 375 ± 25°F	No restrictions
Maximum surface temperature of coated parts	450°F	950°F
Use on titanium substrates	Restricted because of potential for solid metal embrit-tlement	No restrictions
Use on parts contacting fuel, food, or drinking water	Not allowed	No restrictions
Preload torque requirements for threaded fasteners	Standards are based on cadmium electro- plates	Substantially more torque is required
Coated parts requiring solder- ing	Superior adherence of solder to coating	Restricted due to adherence of solder

Torque Requirements

Past studies have documented the fact that more torque is needed to achieve the same tension on aluminum-plated fasteners than on cadmium-plated fasteners. The difference is large enough that aluminum- and cadmium-coated fasteners cannot be used interchangeably. Two reports present data that compares torque requirements for Ivadized aluminum-plated and cadmium-electroplated nut and bolt combinations. The average torque required to produce a 20,000-pound load was found to be up to 35 percent higher for aluminum-plated fasteners than for cadmium-plated fasteners. The average torque for the cadmium-plated combinations was 600 inch-pounds while the average

for the aluminum-plated fasteners was 811 inch-pounds. The results of these tests indicate that AIVD aluminum cannot be substituted for cadmium as a fastener coating without revising torque requirements, plating procedures, lubrication practice, or some combination of all three.

The Pensacola Naval Air Station applies AIVD aluminum coatings on fasteners used on helicopter rotor heads. Torque differences between these aluminum-plated parts and the cadmium-plated parts are minimized by using a thin coating (0.3 mil, Class 3 aluminum coating), by peening the coating with glass beads, and by using a cetyl alcohol lubricant. The Naval Station has found that AIVD coatings applied at a slower than usual rate minimizes variations in plating. Although more than normal effort and attention is required during plating and assembly, torque differences are kept at acceptable levels by these operational practices.

McDonnell-Douglas tested a very thin AIVD coating (0.15 to 0.17 mil) on five nut and bolt combinations.² (The minimum thickness is 0.3 mil for a Class 3 coating.)

Torque requirements for these thin coatings were lower than for normal AIVD coatings, but were still greater than those required for electroplated cadmium fasteners. The test results indicated that torque requirements for the thin AIVD coatings could not be confidently maintained within the ±25 percent range specified for the cadmium electroplates.

A 50 percent synthetic graphite in petrolatum lubricant was used during almost all of the McDonnell-Douglas tests involving both aluminum and cadmium fasteners. Additional investigations indicated that solid dry film lubricants, which incorporate either molybdenum disulfide or graphite in a resin binder, might bring torque requirements for AIVD coatings to within the range of cadmium-plated fasteners.

DEMONSTRATION TESTS AT ANAD

Summary of AIVD Performance

Demonstration tests of a full-scale AIVD system were conducted at ANAD between October 1990 and April 1991. The primary objective of the demonstration test was to determine if AIVD is a viable alternative to cadmium electroplating at ANAD.

A secondary objective was to develop the operating skills of AIVD operators.

Additionally the tests were used to establish operating parameters such as wire feed rate and boat speed necessary to achieve reproducible coatings that satisfy specifications regarding coating thickness, adherence, corrosion protection, and appearance.

Eighty-six types of parts used on Army vehicles and engines were successfully plated during the tests. Additionally, numerous nuts, bolts, brackets, and other small parts were successfully plated using a barrel coater. On a few occasions, applied coatings did not meet thickness specifications. Operating conditions and methods were changed in order to achieve compliance. These changes included extending plating times and plating in two stages, with rotation of parts between stages.

The Military Specification for Aluminum Ion Vapor Deposition Coatings differentiates between Type I coatings that are as-is and Type II coatings that receive a chromate conversion coating. The Ivadizer operating procedures are identical for Type I and Type II coatings, and a satisfactory chromate conversion coating was routinely applied to aluminum coatings. Therefore, Type I and Type II coatings are similar with the exception of salt spray corrosion resistance requirements.

Five aluminum-coated parts were tested in a salt spray cabinet; satisfactory results were obtained on four of the five parts. The fifth part (Part No. 11683952, Connector, Male) had a hollow male connection at a 45-degree angle to the base. Corrosion was detected inside the connection. In subsequent tests, the interior of the connection apparently received better coating when the hollow was positioned perpendicular to the plating boats.

The Military Specifications require that test coupons be used to monitor both aluminum- and cadmium-plating operations. A test coupon is a thin metal sheet that can be tested in lieu of the actual parts either when destructive testing is required or when the parts cannot be tested as a result of shape or size. Typical test coupons are mild steel sheets 4-in.-by-1-in. and 0.040-in.-thick or 6-in.-by-3-in. and 0.040-in.-thick. Because the coupons are flat and do not have sharp angles, cavities, or recessed areas, they are easier to plate with minimum variations in thickness than are actual parts. Therefore, thickness measurements were made, whenever possible, on the actual parts.

A cadmium electroplate on a part may appear satisfactory visually but provide insufficient protection. This can occur if the uniformity of the plating varies significantly as a result of the configuration of the part. Some areas may receive less-than-adequate plating but not be detected visually and ultimately may fail in service. A benefit of the AIVD process is that it virtually eliminates such false-positive visual test results. After the aluminum coat has been applied, peening with glass beads is used to densify the coating and provide a shiny metallic surface. Aluminum coatings that withstand this glass bead preening without flaking or peeling have passed a more stringent adhesion test than the visual test called for in the specifications. A poorly coated aluminum part is unlikely to pass the peening process and be put into field service.

Scrap parts and test coupons were tested in the salt spray cabinet, and all items tested, with the exception of the male connector mentioned previously, passed both adhesion and corrosion resistance testing.

Removable internal shields placed in the chamber are used to block the flow of aluminum vapor and protect the boat clamps, electrodes, wire feed mechanisms, and chamber walls. Accumulated aluminum must be periodically removed from the shields. A caustic solution can be used, but the spent caustic from this cleaning is a corrosive waste. This waste generation can be minimized by painting a slurry of boron nitride (which serves as a release agent) on the shields. The accumulations then can be more easily removed without caustic stripping. The boron nitride treatment cannot be used, however, where aluminum could fall off the shields and into the boats, as this would interfere with the boat operation. Overall, the use of boron nitride reduces the frequency and amount of chemical cleaning required.

COST OF ALUMINUM AND CADMIUM COATINGS

Capital Cost

Table 5 presents installed capital costs of an AIVD system and a cadmium electroplating facility. Estimated capital costs are \$1,025,000 for the AIVD system and

TABLE 5. CAPITAL COST COMPARISONS BETWEEN ALUMINUM COATING AND CADMIUM ELECTROPLATING

Item	Cost
AIVD	
Ivadizer Model HR72X144	\$437,500 ^a
Two additional parts coating racks	57,600 ^a
Barrel coating parts rack	28,500 ^a
Two grit blasting cabinets	77,000 ^a
Cryogenic cooling system	35,000 ^a
Two glass bead preening cabinets	77,000 ^a
Recommended spare parts	40,900 ^a
Manufacturer's installation and training	92,200 ^a
Customer-supplied facility modification and freight	179,300 ^b
TOTAL CAPITAL COST	\$1,025,000
Cadmium Electroplating	
1100-gal. automatic cadmium- electroplating system	\$310,000 ^C
Two 1800-gal. cadmium-plating lines	100,000 ^C
Three 480-gal. cadmium-plating lines	60,000 ^C
Customer-supplied facility modifications and freight	130,000 ^b
TOTAL CAPITAL COST	\$600,000

^a Actual price of AVID system installed at ANAD.

b Estimate.

c Vendor quote.

\$600,000 for the cadmium-plating facility. These capital cost estimates do not include degreasing, cleaning, stripping, and rinsing facilities that are common to both systems. The cost estimate for the AIVD system is based upon the actual costs incurred during this project for installation of the system at ANAD. The cadmium-plating cost estimate is based upon estimates from vendors for a facility equivalent to that currently in place at ANAD.

The estimated cost of the cadmium plating facility is based upon current regulations. More stringent regulatory requirements would, at best, significantly increase capital costs and, at worst, render cadmium plating infeasible. For example, state regulations have eliminated most cadmium electroplating at Red River Army Depot and at Jacksonville Naval Air Station. Present regulatory requirements coupled with the prospect of more stringent future requirements would probably make AIVD the preferred choice over cadmium electroplating for a new facility. The choice facing most Army installations, however, is whether to replace an existing cadmium plating facility with AIVD. Retrofitting a cadmium plating facility to achieve zero discharge standards would be expensive, and the cost would be very situation-specific. For a facility the size of ANAD, the estimated cost could be between \$300,000 and \$400,000.

Annual Cost

The cadmium-plating facility at ANAD can plate about 490 ft² of metal surface per 8-hour shift (61 baskets of parts at 8 ft² per basket) with a normal production rate of about 320 ft² per shift (40 baskets at 8 ft² per basket). The AIVD system as installed had a capacity of about 144 ft² per shift. It is estimated that about \$100,000 of equipment modifications would be required to increase this rate to about 200 to 250 ft² per shift. (These modifications have been included in the capital cost estimate.) For comparison, a commercial job shop visited during the study that had made numerous modifications to increase productivity could coat about 270 feet of metal surface in an 8-hour shift.

Table 6 presents estimated annual costs of an AIVD system and a cadmium-electroplating facility. Estimated annual costs per square foot plated are \$6.64 for aluminum

TABLE 6. ANNUAL COST COMPARISONS BETWEEN ALUMINUM COATING AND CADMIUM ELECTROPLATING

Annual Costs of AIVD	
Day shift labor, 3 people, \$20/h, 2080 h/year	124,800
Night shift labor, 3 people, \$22/h, 2080 h/year	137,280
Maintenance, 2% of capital cost	20,500
Utilities, \$10/h, 3800 h/year	38,000
Wire, \$6.50/h, 3800 h/year	24,700
Boats, \$9/h, 3800 h/year	34,200
Capital recovery, 9%, 15 years	125,850
Total Annual Cost	505,330
Cost plated, \$/ft ²	6.64
Annual Costs of Cadmium Plating	
Day shift labor, 3 people, \$20/h, 2080 h/year	124,800
Maintenance, 2% of capital cost	12,000
Utilities, \$1/h, 1900 h/year	1,900
Cadmium metal, \$5.015/lb, 2500 lb/year	12,540
Sodium cyanide, \$1.15/lb, 1600 lb/year	1,840
Capital recovery, 9%, 15 years	73,670
Hazardous waste disposal, 14,700 lb at \$0.50/lb	7,350
Wastewater treatment, 250,000 gal/year at \$0.365/gal	91,250
Employee cadmium exposure monitoring	6,400
Blood tests for cadmium	3,000
Increment annual physical exam costs	6,000
Total Annual Costs	340,750
Cost plated, \$/ft ²	4.47

and \$4.47 for cadmium. (These costs do not include degreasing, cleaning, stripping, and rinsing facilities that are common to both systems.) In each case, it was assumed that 76,160 ft² is plated per year. The AIVD system would operate two shifts per day to achieve this production rate.

ANAD's cadmium-plating facility has an advantage in that the wastewater generated can be treated in the depot's IWTP. A zero discharge system would have higher capital and operating costs. The table shows that about one-third of the annual costs for cadmium plating are attributable to hazardous waste treatment and disposal and employee protection. These costs will increase whenever more stringent standards are imposed. For example, the expected reduction of the OSHA standard for employee exposure to cadmium will generate additional costs resulting from more stringent employee and area monitoring requirements. Such developments could reduce or eliminate the cost differential between aluminum plating and cadmium plating.

Summary of Findings

The AIVD Demonstration Test Program conducted by USATHAMA provided the following results:

- Depot personnel could satisfactorily coat all parts tested.
- Aluminum coatings provided at least equivalent corrosion protection compared with cadmium electroplates.
- Aluminum coatings had satisfactory adherence to the base metal.
- Torsion testing of threaded fasteners demonstrated that aluminum-coated fasteners required substantially greater applied torque than did equivalent cadmium-coated fasteners.
- Based on the test, ANAD personnel have recommended AIVD coatings as an optional coating for Model 1790 engine components.

Replacement of cadmium electroplating with the AIVD technology will significantly reduce generation of cadmium-contaminated wastes at ANAD. In most cases, this technology could be substituted directly for cadmium electroplating and would

require minimal changes in pretreatment or posttreatment procedures. Pretreatment of parts with welded surfaces and recessed areas may require modification to include preheating to eliminate outgassing from trapped moisture. Posttreatment changes would include lubrication of threaded parts prior to assembly as well as separation from cadmium-plated fasteners, particularly for parts with critical torque requirements.

Additionally, parts with recesses more than one diameter deep (two diameters deep if open at both ends) and where the interior must be coated will require another coating technique for the interior as AIVD cannot coat these recesses. Three classes of alternative coatings are:

- Aluminum-filled MIL-C-81517 base coats
- Ceramic sealcoats
- Primers, topcoats, and sealants

The aluminum-filled base coats are paint-type materials that contain suspended aluminum metal. The aluminum-filled coating becomes electrically conductive when either heat-cured or burnished with glass beads. The aluminum coating then provides sacrificial corrosion resistance. The ceramic sealcoat is a painted-on protective coating that is usually heat-cured. It forms a solid film and is often used on top of aluminum-filled base coats. Primers, topcoats, and sealants provide solid film protective coatings. Materials used include epoxies, polyurethanes, and sprayable sealants.

As a result of the demonstration tests, ANAD personnel have proposed that AIVD coatings be made an acceptable alternative to cadmium electroplates. The substitution requires the approval of the Army Tank Automotive Command. Depot personnel have identified about 450 vehicle and engine parts that are suitable for aluminum coatings in place of cadmium electroplates.

Total replacement of cadmium electroplating by aluminum vapor deposition would eliminate the generation of about 15,000 pounds of RCRA-listed hazardous wastes and 250,000 gallons of wastewater annually. However, the current cost of Ivadizer coatings is estimated to be about 50 percent greater than cadmium electroplates. The cost of operating cadmium-plating lines will continue to increase because of increasingly more

stringent regulations, while the cost of Ivadizer coatings should decrease as the technology matures.

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HOT-GAS SAMPLING AND ANALYSIS SYSTEM FOR USE IN THE CONE PENETROMETER

by

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ABSTRACT

A hot-gas sampling and analysis system is proposed as a potential sensor for use in the Site Characterization and Analysis Penetrometer System (SCAPS). A bench-top, prototype model was evaluated by using a Thermogravimetric Analyzer coupled with a Fourier-Transform Infrared Spectrometer (TGA/FTIR). The procedure consists of exposing a sample (0.1-100 mg) to a controlled atmosphere (N2, dry air, etc.) while heating it at a controlled rate (10°C/min to 100°C/min). The sample compartment of the TGA is continuously purged so the gases from thermal decomposition and/or evaporated can be transported to a light tube for analysis by FTIR. This method shows potential at detecting various contaminants in soil and groundwater, including fuels, petroleum hydrocarbons, explosives, and chlorinated solvents. Preliminary results using this technique for soils spiked with explosives and explosive byproducts demonstrate the potential for in-situ detection of these contaminants.

INTRODUCTION

The Site Characterization and Analysis Penetrometer System (SCAPS) has developed into a viable technology for detecting and delineating fuel, oil and lubricants (POL) in various soils based on the fluorescence of aromatic and polycyclic aromatic hydrocarbon compounds. One of the objectives of SCAPS program has been to develop sensor systems which can be adapted to the cone penetrometer equipment commonly used on soils. This system has already been successfully used at a number of sites for detecting soils contaminated with 20,000 ppm (parts per million) to 200 ppm of spilled or leaked POL products (1-4). The current laser-induced fluorescence sensor is limited to specific compounds and not able to directly detect a wide range of contaminants like explosives and chlorinated solvents that do not fluoresce.

Although the detection limits using field fluorescence are not as low as laboratory analytical techniques (example-GC/MS), SCAPS provides on-site, in situ information about the location, migration, and concentration of POL contamination. When compared to the commonly used techniques of drilling, sampling and laboratory testing, SCAPS provides information in hours, instead of weeks. As with any evolving technology, the actual field operation has shown areas in which improvements and enhancements can be made. One such improvement is a more versatile sensor to handle a wider range of contaminants. A hot gas analyzer is proposed as a possible sensor system. Instead of analyzing or sensing the contaminant in place in the soil, a high temperature (over 200°C) inert gas is used to heat a soil sample in place and collect the volatiles. These volatiles are transferred by the flowing gas to the surface for realtime analysis at the site. In this work, the system used to determine the constituents of these evolved gases is a Fourier-Transform Infrared Spectrometer (FTIR).

FTIR provides a versatile technique for analyzing these contaminants (5). All hydrocarbon compounds have some bands absorbing in the mid-infrared range $(4000~{\rm cm}^{-1}$ to $400~{\rm cm}^{-1})$. The analysis of gases using FTIR has been applied to monitoring smoke stack emissions and passive-remote FTIR for

detection of suspect chemical plumes (6). Open-path infrared spectrometers have been researched as a technique for determining the origin, identity, and concentration of volatile organic compounds (VOCs) being emitted from the soil at contaminated sites (7).

Thermogravimetric analysis equipment used with FTIR provides a method to perform controlled heating experiments on contaminated soils and determine the major constituents coming out of the sample under specific conditions. The TGA provides a method for measuring the weight loss and purging the volatile materials to a FTIR light pipe for identification. For instrument development purposes, the TGA is being used as a bench testing system to develop the data needed to design the penetrometer probe that will furnish the heat and flowing gas to purge soil sample in the subsurface and produce gas/vapor samples for analysis. In the preliminary work, analysis of the volatiles was performed with the FTIR, but future plans call for using a variety of analytical systems including mass spectroscopy and gas chromatography.

CONFIGURATION OF THE TEST SYSTEM

A schematic of the TGA/FTIR analyzer unit is shown in Figure 1. The system consist of a TA Instruments (New Castle, DE) TGA 50 and Nicolet (Madison, WI) 510P FTIR. The FTIR consists of a TGA interface in a Nicolet Auxiliary Experiment Module (AEM). The beam of infrared energy is reflected into the light tube with a pathlength of 200 mm and the resulting energy is collected in a mercury-cadmium telluride-B detector (MCT-B) (Figure 2).

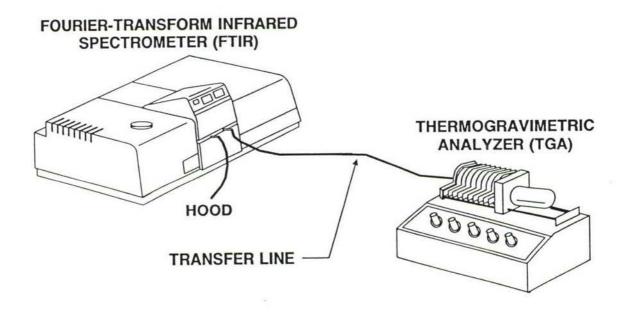


Fig. 1. Schematic of TGA/FTIR experimental setup.



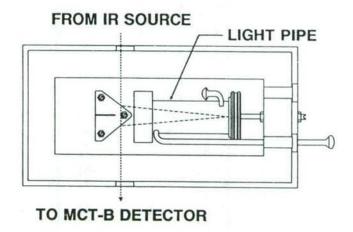


Fig. 2. Overhead view of the TGA interface.

Before data collection, a series of collection parameters and experimental conditions must be prescribed. Using the instrumentation software, the FTIR is set up to coadd every 16 scans with a resolution of 8 cm⁻¹ over a time period of 15 minutes. The spectral information is then stored in a plot of spectral intensity versus time. Once the background spectra have been selected, (these include only moisture and CO₂) a Gram-Schmidt reconstruction is produced. The Gram-Schmidt reconstruction is the main source for retrieving spectral information at specific experimental times (See Figure 3). Another form of data is the chemigram. A chemigram is the spectral intensity of a certain functional group or groups over a specified time range. This gives the user information about when these constituents are detected by the system. For the TGA, the primary source of information is the thermogram. The thermogram shows the percent weight loss of the sample versus temperature or time. This information is provided on a realtime basis.

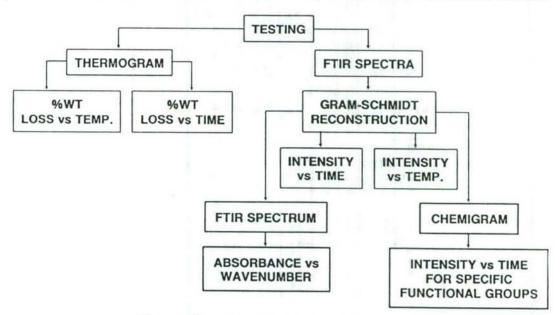


Figure 3. Flowchart of data analysis.

The experimental procedure established for these tests consisted of exposing the sample to heating that ramped from an equilibrium temperature of 30°C to 500°C at 20°C/min or 50°C/min while the TGA sample compartment was purged with $\rm N_2$ at a flow rate of 330 ml/min. The TGA interface in the FTIRAEM was kept at a temperature of 230°C±1°C to prevent the condensation of the gases in the light pipe.

A sample (contaminant or soil with or without contaminants) weighing between 0.1 and 100 mg was placed in the microbalance of the TGA. The sample was quickly heated to an equilibrium temperature of 30°C and then heated over a programmed rate. Once the sample started to decompose and/or volatiles came off the system, these constituents were purged with a gas (N2 or dry air) and transferred through an insulated line to a module interface of a Nicolet 510P FTIR. The gases were collected in a light pipe for analysis with the FTIR. A Gram-Schmidt reconstruction was then created which showed the relative intensity of the signal for the spectra versus either time or temperature. The shape of the Gram-Schmidt plot was used to determine major groups of decomposition products. A spectrum at a temperature where there was a significant amount of water was used to subtract out the contribution of the water.

In this initial work, 2,4,6, Trinitrotoluene (TNT), 2,4 Dinitrotoluene (2,4 DNT) or 2,6 Dinitrotoluene (2,6 DNT) was selected as the contaminant and added to natural sandy-clayey soils. Spectra of the pure TNT, 2,4 DNT and 2,6 DNT were first obtained to determine the types of decomposition products in $\rm N_2$ and dry air.

RESULTS AND DISCUSSION

TGA/FTIR of 2,6 DNT and 2,4 DNT

The initial work consisted of determining the exothermic decomposition temperature and/or the vaporization temperature for 2,6 DNT and 2,4 DNT samples. Since the actual decomposition temperature is very dependent on the purity of the sample and experimental conditions, only approximate temperature ranges were desired. Samples of 0.3540 mg, 0.9390 mg, and 4.1050 mg of 2,6 DNT were placed in the TGA sample compartment. Figure 4 shows the resulting thermograms for these three samples. Although running samples smaller then 5 mg is not recommended, these small samples were run to determine the sensitivity of the instrument and the temperature of total weight loss of the sample. The samples started volatilizing between 60°C and 80°C and complete weight loss was noted around 145°C, 160°C, and 190°C for the three samples. These temperatures are lower then values found in the literature for decomposition (8).

The evolved gases were simultaneous analyzed in the light pipe with the FTIR. A typical FTIR spectrum for a 0.9390 mg sample of 2,6 DNT taken after 8.93 minutes is shown in Figure 5. The prominent peaks at 1550.97 cm⁻¹ and 1358.06 cm⁻¹ represent the N=O stretching of the NO₂ groups. The band at 700 cm⁻¹ is from the C-H ring bend of the 1,2,3 tri- substituted benzene ring. When compared to the spectrum of a 1.2460 mg sample of 2,4 DNT taken after 12.43 minutes, several differences are noticeable (Figure 6). First, the NO₂ peak at 1550.97 cm⁻¹ contains a shoulder not visible in the 2,6 DNT sample. A second difference is the presence of a band at 833 cm⁻¹ from the C-H bend of a 1,2,4 tri-substituted benzene ring. These differences make identification of the different explosive byproducts possible if the sample size is sufficiently large.



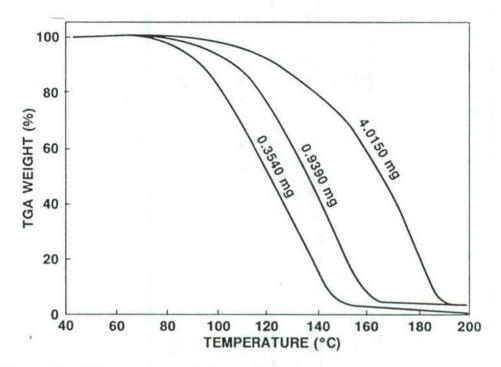


Figure 4. Thermograms of for various sample weights of 2,6 DNT.

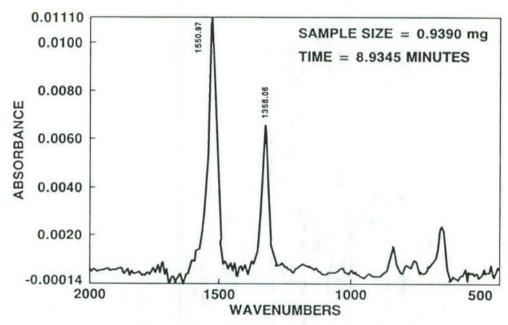


Figure 5. FTIR Spectrum of 2,6 DNT.

Figure 7 displays the FTIR spectrum of 0.3540 mg of 2,6 DNT after 9.87 minutes. The only absorbance bands which appear above the background noise are the N=0 stretching bands at 1550 cm $^{-1}$ and 1350 cm $^{-1}$. Samples weighing significantly less than 1.0 mg have too low a signal to noise ratio to clearly identify anything other than the strongest absorbing bands.

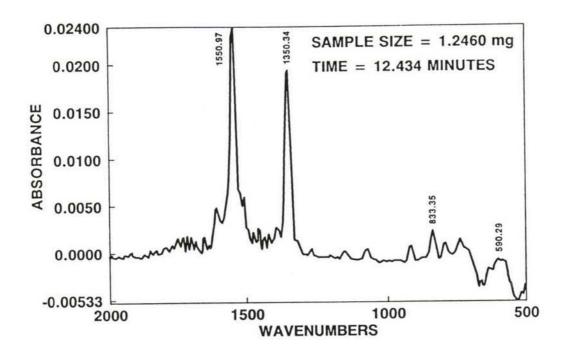


Figure 6. FTIR Spectrum of 2,4 DNT.

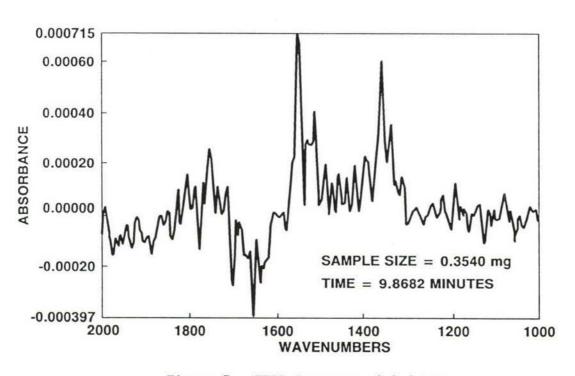


Figure 7. FTIR Spectrum of 2,6 DNT.



Only one soil contaminated with 2,6 DNT has been investigated. This sample consisted of 2.3% (23,000 ppm) of 2,6 DNT in a soil. A spectrum of the evolving gases are presented in Figure 8. It is apparent that all the distinguishable peaks are present and work is currently being performed on samples of much lower concentrations (<500 ppm).

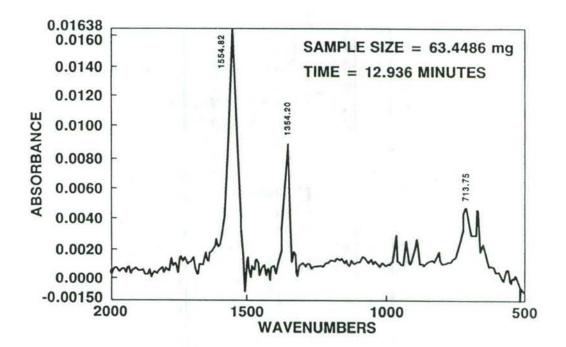


Figure 8. FTIR spectrum of evolved gases from soil spiked with 2.3 wt% 2,6 DNT.

TGA/FTIR of TNT

A limited number of tests were also run on a kaolin-type soil containing 3500 ppm of TNT. These tests were run using dry air as the purging gas and produced interesting results. Figure 9 displays the Gram-Schmidt reconstruction and the thermogram for this sample. The thermogram is not sensitive enough to pick up the weight loss associated with the TNT, but does show significant weight loss at temperatures from 160°C to 280°C. Figures 10 and 11 display the effect of subtracting the moisture on the resulting spectra. This process reduces the contribution of moisture drastically and allows for easier detection of the remaining evolved gases. The only noticeable evolved gas from the TNT contaminated sample nitrous oxide (NO). The characteristic band appeared at around 2200 cm⁻¹ (Figure 12). There was also several smaller bands at 1250 cm⁻¹ and 700 cm⁻¹. It is evident from the evolving gases that 2,4,6 TNT in the presence of air is decomposing into smaller compounds, like NO.

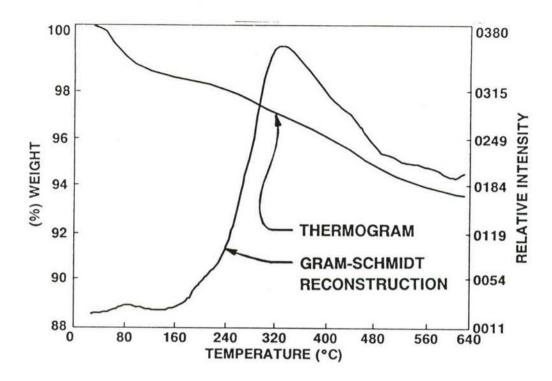


Figure 9. Gram-Schmidt reconstruction and thermogram for soil spiked with 3500 ppm of TNT.

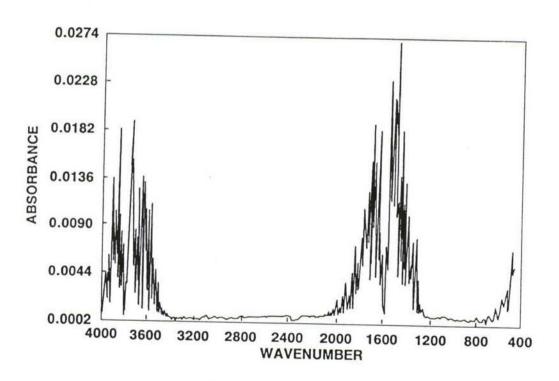


Figure 10. FTIR spectrum of evolved gases at 83°C.



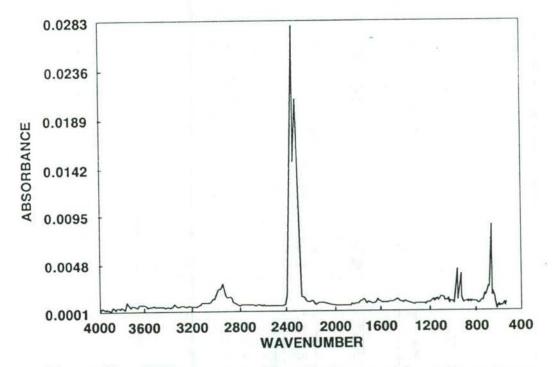


Figure 11. FTIR spectrum of evolved gases minus the moisture.

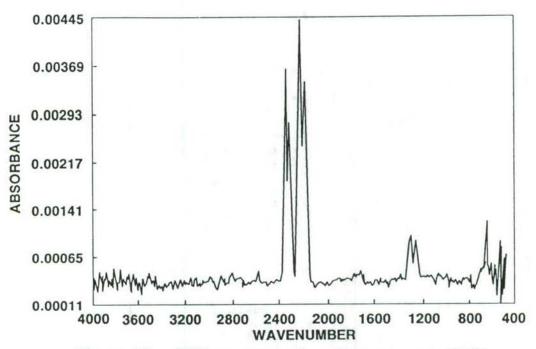


Figure 12. FTIR spectrum of evolved gases at 201°C.

CONCLUSIONS

1. Preliminary results show that when 2,4 DNT and 2,6 DNT are heated with an inert gas (30° C to 500° C), the evolved gases consist of pure 2,4 DNT and 2,6 DNT. The FTIR spectra of the different explosive byproducts were easily identifiable if a sufficient gas sample was in the light tube.

- 2. The minimum operating size of this test system is approximately 1 mg of sample.
- 3. Further work is required in reducing the detection limit of the system, analyzing other contaminants in soils like chlorinated hydrocarbons, HMX, and RDX, and developing a prototype heated probe sampler to fit onto the cone penetrometer equipment.

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SENSOR TECHNOLOGY FOR THE CONE PENETROMETER

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ABSTRACT

Improvements in the ability to map contamination in soil and ground water are being made by adapting novel types of sensors to the penetrometer and by developing new methods of interpreting data obtained from existing sensors. The Site Characterization and Analysis Penetrometer System (SCAPS) currently uses a fiber optic fluorometer and a DC electrical resistivity instrument as the major contaminant sensor systems. Initial efforts at evaluating new technology indicate the feasibility of developing a Fourier Transform Infra-red (FTIR) spectrometer for use with the cone penetrometer. An FTIR spectrometer operating from 4000 cm⁻¹ to 600 cm⁻¹ can be especially useful in distinguishing different types of organic contaminants (especially compounds in fuels and energetics) in soil. Preliminary tests done with FTIR using attenuated total reflectance (ATR) indicate that hydrocarbons in fuels can be detected down to approximately one percent by weight in simulated soil matrices.

Trials with a fiber optic reflectometer measuring color development on a chemical indicator have demonstrated that colorimetric analytical techniques can be used to detect and measure a wide variety of contaminants in soil. The proposed system is based on a fiber-optic reflectometer that can detect color changes when suitable reagents are brought into contact with the soil.

Existing sensor technology can be exploited by using statistical approaches to evaluate several interrelated soil characteristics. When estimates of soil type obtained from soil strength measurements are combined with soil electrical resistivity measurements, the composite characteristics can be used as an index of contamination of the soil. The index produced using multivariate statistical techniques can be used to classify soil intervals as contaminated or uncontaminated when the separate measurements can not produce a clear picture.

INTRODUCTION

Since 1986, the U. S. Army Toxic and Hazardous Materials Agency (USATHAMA) has sponsored the development of technology that allows a cone penetrometer to be used in the investigation of hazardous waste sites. This research has been resulted in the development of a specialized Site Characterization and Analysis Cone Penetrometer System (SCAPS). One important aspect of this work has been the adaptation of existing sensors or the production of new sensors that could be incorporated into the cone penetrometer to allow the system to determine soil characteristics and detect contaminants in soil as the penetrometer rod is forced through the soil.

The conventional cone penetrometer, that is standard in civil engineering foundation and roadbed investigations, consists of a 35-mm diameter instrumented steel rod that is forced into the soil using hydraulic rams that work against a large reaction mass or against earth anchors. The most common configuration for a cone penetrometer is a large 20 to 30-ton truck with the hydraulic rams and the power plant mounted aboard so that the rod can be forced into the ground using the truck and its associated equipment as a reaction mass. The SCAPS truck (Fig. 1) is designed around this basic concept but includes modifications for operations on hazardous waste sites.



Fig. 1. Photo of SCAPS truck. The forward compartment houses the hydraulic rams and racks of penetrometer rods. The rear compartment houses the instrumentation.

The guidelines for collecting soil strength data with the standard penetration tool, with a 60-degree conical tip, calls for forcing the cone into the ground at a rate of 2 cm/sec (ASTM, 1991). The soil strength measurements made by measuring the tip resistance and the friction against an instrumented section of the rod wall (the sleeve) are the primary data that the cone penetrometer collects. The soil strength measurements can be used to estimate the grain-size distribution of the particles in the soil if the soil is not overcompacted or cemented (de Ruiter, 1981; Campanella and Robertson, 1982; Olsen, 1988). Soil strength data from the cone penetrometer is typically used to map the distribution of soil types beneath a site. When sensors for other soil properties, such as electrical resistivity, fluorescence or reflectance are added, the penetrometer can become a valuable tool for the investigation of contaminant distribution in the subsurface (Lurk and others, 1990, 1991; Malone and others, 1992).

The purpose of this paper is to explore possibilities of incorporating new sensor technology in the cone penetrometer and to examine ways in which output from separate sensors can be combined to produce improved data interpretation. The initial efforts at producing new sensor systems have concentrated on developing techniques that are useful in rapidly screening a site for contamination using sensors that respond rapidly enough to allow the penetrometer to move at the usual speed of 2 cm/sec. Sensor development in the SCAPS program concentrates on finding useful indicators of the presence of contamination. Many sensors measure soil characteristics that are related to the presence of contamination but may not measure the concentration of the contaminant directly and quantitatively. The goal of the SCAPS system, as presently employed, is to locate areas where soil and ground-water samples are to be collected for detailed analyses.



INFRARED SPECTROSCOPY FOR THE SCAPS SYSTEM

Fourier-Transform Infrared Spectroscopy (FTIR) using Attenuated Total Reflectance (FTIR-ATR) is currently being evaluated as a possible sensor for the SCAPS system. FTIR-ATR provides several advantages over existing sensors in its capability to rapidly detection and identify of a wide range of non-fluorescing contaminants in soil. The major technical barrier that restricts the use of FTIR is the limited availability of optical waveguides capable of transmitting infrared energy (4000 cm⁻¹ to 600 cm⁻¹) over long distances (greater than 100 m). With the development of new fiber optics materials based on heavy metal fluorides and heavy metal oxides this problem should be alleviated.

A schematic of the FTIR-ATR technique is shown in Figure 2. As an infrared beam of energy is reflected into the internal reflectance element (IRE), the beam travels between the IRE and the sample. If the refractive index of the IRE is greater than the sample, the beam of energy will pass through the IRE/sample interface and into sample. The energy with the same frequencies as the vibrational modes in the molecules will be absorbed into the sample. Once the infrared beam has passed completely through the IRE, the energy is collected and the amount absorbed versus wavenumber (inverse of wavelength) is plotted. A spectrum is produced from the ratio of the background containing only the IRE and the IRE/sample signal.

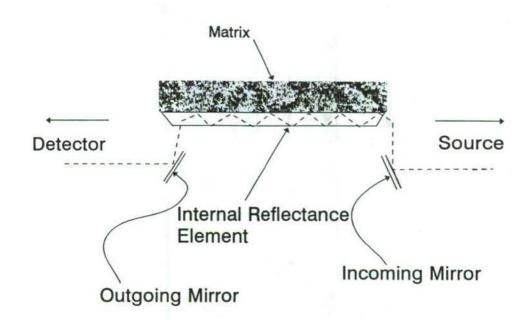


Fig. 2. Schematic of an FTIR system using attenuated total reflection. The system would be the preferred design for the SCAPS system because of the speed of data acquisition.

Preliminary work performed on the FTIR-ATR has concentrated on simulated soil matrices made of glass beads. The initial tests were conducted to determine the operating range of the FTIR, the detection limits, and the limiting matrix effects. The glass beads tests are especially useful in determining the relationship between signal strength and particle size. Glass beads represents a system where the contaminant will not migrate into the matrix, but absorb on the surface. The matrices were spiked with fresh jet aircraft fuel (JP-4) as the test contaminant.

To determine the effect of grain size on the signal strength of the absorbing bands in the mid-infrared, several different diameters of glass beads were selected. A plot of the absorbance maximum of the absorption bands between 1200 cm⁻¹ and 800 cm⁻¹ versus bead diameter is presenting in Figure 3. In the band shown here, the IR absorption is due to the glass only, no contamination is present. Note that the signal strength increases with decreasing bead diameter, while the standard deviation within each set of three identical runs on the same diameter beads increased. These effects can be attributed to the effective contact area available for penetration of the infrared beam. The larger particles (approx. 400 microns or micrometers) have a much smaller contact area on the IRE. These initial tests indicate that when particles in the soils are greater than some nominal diameter, there will be inadequate contact for the IR beam to penetrate into the sample.

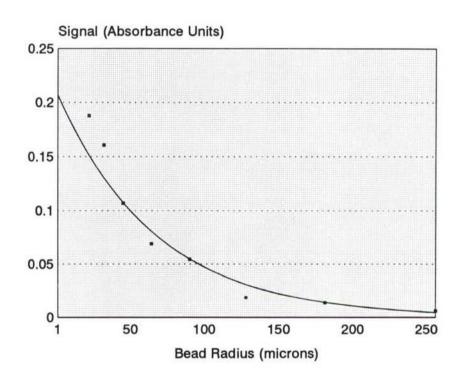


Fig. 3. Plot of the absorbance maxima between 1200 cm^{-1} and 800 cm^{-1} versus bead diameter for clean glass beads. As the bead diameter increases the absorbance decreases.

Figure 4 shows the spectra of glass beads contaminated with 1.0%, 2.5%, and 20% JP-4. A ratio of the maximum absorbance of the symmetric C-H bending between 1600 cm $^{-1}$ and 1400 cm $^{-1}$ and the maximum absorbance of the inorganic band is used to determine the amount of contaminant. The calibration curve of the absorbance ratio versus weight percent contaminant is shown in Figure 5. A first order equation produced a good fit with a correlation coefficient of r^2 =0.9834. Although these contamination levels are high (10000 ppm and above), the results are useful and work is currently being performed to determine the minimum detection levels.

CHEMICAL INDICATOR TECHNOLOGY FOR THE SCAPS SYSTEM

There are a wide variety of techniques for using changes in the optical characteristics of specific indicator compounds to detect or to quantify specific elements or compounds of interest is water and soil (Feigl, 1958;



Charlot, 1965). The major limitations in using the optical properties of indicator compounds with the optical sensors on the cone penetrometer relate to the problems in releasing an indicator compound into the soil or ground water and in detecting changes in the optical properties of the indicator when the masking effects of soil are present. Work is underway on techniques for overcoming both of these problems.

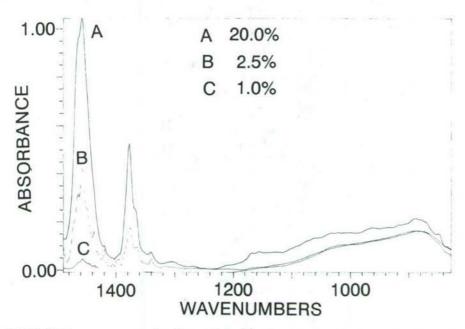


Fig. 4 FTIR-ATR spectra of glass beads contaminated with 1.0%, 2.5% and 20% fresh JP-4.

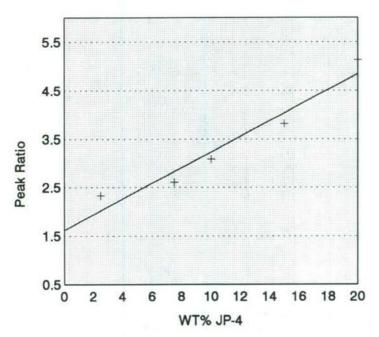


Fig. 5. Calibration curve for FTIR-ATR absorption from JP-4 in a matrix of 25-micrometer diameter glass beads. Absorption peak maxima at 1450^{-1} are plotted.

Initial trials have been made using the indicator system with the colorimetric reaction that occurs when 2, 4, 6, trinitrotoluene (TNT) in aqueous solution is treated with alkali (Zhang and others, 1988). The colored complex that forms is a hydroxy complex of TNT that absorbs strongly between 460 and 520 nm. The test was conducted by preparing a chemical indicator on a white absorbent by wetting the absorbent with a 50% solution of sodium hydroxide and allowing the absorbent to air-dry at room temperature (23° C). The tests with the chemical indicator system were conducted with a fiber-optic probe developed for measuring optical characteristics in soil. The configuration of the probe is described in Lieberman and others (1990). data were collected with a Guided Wave Model 260, fiber-optic spectrophotometer (Guided Wave, Inc. El Dorado Hills, CA). The prepared absorbent was moistened and placed over the optical port in the probe. A plastic hypodermic syringe was cut off at the dispensing end so that a soil sample could be loaded in the barrel of the syringe. By holding the open end of the syringe over the absorbent and pushing in the plunger the soil sample could be forced tightly against back of the absorbent. The soil was forced against the absorbent and the absorbent was pressed against the optical port on the side of the penetrometer rod. This technique mimicked the effect of soil pushing against the absorbent and forcing it against the optical port on the side of the penetrometer as the rod advances into the soil. Moist soil samples were prepared by mixing locally obtained silt (Vicksburg Loess) with distilled water or with a 100-ppm aqueous solution of TNT in distilled water. The characteristic red complex appeared within 10 seconds of the contact of the absorbent with the contaminated soil. No color development was observed in the uncontaminated soil samples. Typical reflected spectra obtained from the spectrophotometer are shown in Figure 6. The colored complex absorbs strongly in the blue. The differences in spectra indicate that TNT at high concentrations (100 ppm) in soil water can be easily detected.

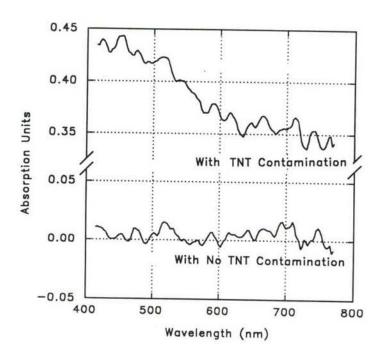


Fig. 6. Reflection spectra obtained when an absorbent containing a base is in contact with clean soil and soil contaminated with a solution of 100 ppm TNT.



No attempts were made in these initial tests with the chemical indicator, to optimize the response of the indicator and lower the detection limit. Simple changes such as moistening the absorbent with a polythylenimine solution or a diluted ethanol solution will enhanced the color development (Zhang and others, 1988).

TNT detection systems other than the alkali color complex reaction can be built into the chemical indicator system. The SCAPS system currently has a fiber-optic fluorometer as soil contamination detector. The SCAPS fluorometer can be modified to permit its use with a chemical indicator and techniques that use fluorescence or fluorescence quenching as a method for detecting explosives and energetics. Techniques based on fluorescence are generally more sensitive than the direct color change methods. Detection limits for the fluorometric techniques are typically below 1 ppm in water (Heller, McBride and Ronning, 1977; Jian and Seitz, 1990; Hurum, Von Wandruszka and Grey, 1991).

COMBINING THE RESULTS FROM MULTIPLE SCAPS SENSORS

The SCAPS system has been designed to make multiple measurements on soil during a single penetrometer punch. Cone resistance and sleeve friction are the primary measurements made with the penetrometer. The soil strength measurements are used to determine the type of soil being penetrated and to collect data on the sequence of soil types beneath a site. In its current configuration the SCAPS can simultaneously make either fluorescence measurements or electrical resistivity measurements in addition to the soil strength measurements.

Soil resistivity measurements made with the cone penetrometer are similar to soil paste resistivity measurements. The cone penetrometer measurements involve the flow of current through three soil pathways acting in parallel:

a) flow through the mineral grain and the fluid between grains.b) flow through and along the surfaces of soil particles primarily

associated with exchangeable cations on the surfaces of the soil particles.

c) flow through interstitial soil solutions.

The soil type primarily influences the second pathway while detecting contaminants involves estimating the effects of the first and third pathways. Soil contamination detection therefore requires the use of an independent method for estimating the percentage of fine particles (primarily clay minerals) in the soil. The strength measurements made with the cone provide an index that relates to the percentage of fines in the soil.

The soil index number is based on a method of interpreting penetrometer data described by Olsen (1988) and programmed by Olsen at WES for use on a microcomputer. The index number represents an estimate of the soil type with 1 corresponding to a clay soil and 5 corresponding to a sand. Intermediate values indicate intermediate gradations or mixtures.

In order to evaluate the ability of a sensor-equipped cone penetrometer to detect contaminated soil, data on soil type and soil resistivity were collected at a former fuel storage/transfer facility on a government installation in Northern Florida (U.S.). The area is underlain by mixed quartz and carbonate sand and the watertable is at a depth of approximately 1.5 m. The soil contamination at the site consists of sludges that were removed from fuel storage tanks and buried at the site as well as fuel that was leaked and spilled during approximately 30 years of operations.

The resistivity and soil index (soil type) data collected at 1-cm intervals from a 1.5- to 3-m depth are plotted in Figure 7. In all samples there is a general trend for the resistivity to increase as the soil index increases (median grain size increases). The soils in penetrometer holes

CPT03 and CPT25 were determined to be contaminated with fuel tank wastes from field fluorometer measurements. In the 1.5-m thickness investigated the contamination levels were estimated to vary irregularly from less than 100 ppm to over 5,000 ppm hydrocarbon. The soils in CPT05 and CPT17 showed no evidence of contamination.

The plot in Figure 7 shows that generally for a given grain size (as indicated by the soil index) the contaminated soils will have a lower soil resistivity. This effect could be caused by lubrication of the friction sleeve by the hydrocarbon contaminants, thereby moving the soil index numbers to higher numbers or it may be caused by decreased resistivity due to the ionic decomposition products from the hydrocarbon contamination. The magnitude of the variation will change with the type of contaminant present and the resistivity of the uncontaminated pore water. The basic trend indicates that the cone penetrometer equipped to measure soil type and soil resistivity can function as a contaminant detector if the measurements are used together.

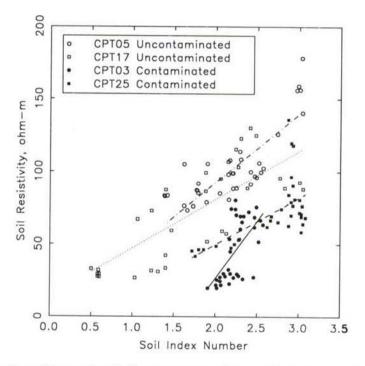


Fig. 7. Plot of soil resistivity versus the soil index. Low index numbers indicate fine-grained (clayey) intervals while higher index number indicate coarse-grained (sandy) intervals.

In order to objectively evaluate or classify a soil interval as contaminated or uncontaminated the soil index and the resistivity measurements were combined using discriminant analysis techniques (Davis, 1973) and a system for classifying each sample was developed. For the purposes of this study, the penetrometer pushes for CPT03 (contaminated) and CPT05 (uncontaminated) were used as a learning set and the discriminant function developed from the learning set (Figure 8) was used to classify the soil intervals in CPT25 (contaminated) and CPT17 (uncontaminated). Out of 62 soil intervals in the test set only 6 samples were "misclassified". The "misclassified" samples were all uncontaminated samples that scored close to the discriminant index. All of the contaminated samples were correctly classified.



The work with discriminant analysis demonstrates the value of combining the output from multiple sensors to identify contaminated soil intervals. Multivariate statistical techniques can be used in real time to produce a preliminary identification of contaminated soil horizons using measurements of the soil type and electrical resistivity.

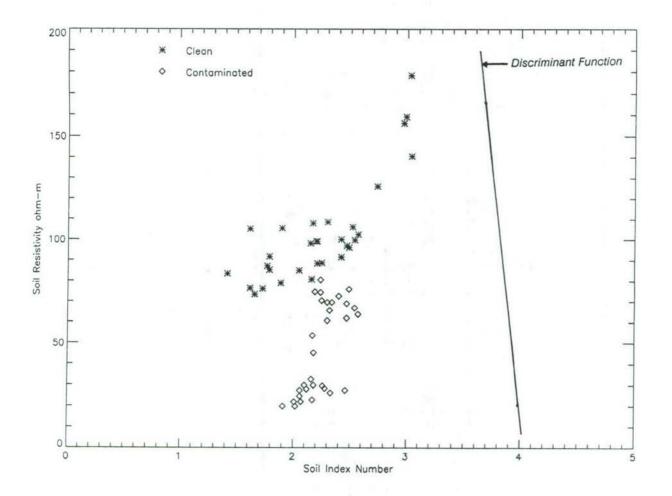


Fig. 8. Plot of soil resistivity versus soil index for a learning set consisting of a contaminated (CPT03) and an uncontaminated or clean (CPT05) penetrometer push through the to of the saturated zone at a fuel storage site. The straight line on the plot is the linear discriminant function.

CONCLUSIONS

Preliminary work with new sensors being developed for use in the penetrometer demonstrated the following:

- a) an FTIR-ATR detection system can be a useful detection system for soil contaminants that have low or no fluorescence. The range of application is restricted by the availability of IR waveguides of practical lengths.
- b) useful data were collected on jet fuel concentrations in simulated soils down to levels of 1% JP-4 by weight with a bench FTIR-ATR system.

- c) the matrix grain size have a significant effect on the absorption measured in simulated soil matrices. The larger the grain size in the matrix the lower the absorption.
- d) chemical indicators can provide a useful system for detecting soil contamination and the color changes can be noted with the fiber-optic reflectometer.
- e) when the soil strength data are used with the electrical resistivity data if is possible to detect the presence of soil contamination from the combined measurement.
- f) multivariate statistical techniques, such as discriminant analysis, can be employed to rapidly produce objective classifications of soils into contaminated and uncontaminated groups.

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STABILIZATION OF HAZARDOUS PAINT BLAST MEDIA

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BACKGROUND

The U.S. Army Depot Systems Command (DESCOM) is one of nine major commands of the Army Materiel Command (AMC). DESCOM operates sixteen depots and depot activities in the continental United These facilities perform repair, maintenance and upgrade operations on all major Army systems including vehicles, weapon systems, and aircraft. DESCOM generated approximately 6.5 million kilograms of hazardous waste in 1989. This amount represents about one-sixth of AMC's total hazardous waste generation. Available data for 1991 indicates that AMC facilities generated 4 million kilograms of hazardous waste from abrasive blasting depaint The majority of this waste originates at DESCOM operations. The cost of disposal for this material was facilities. approximately \$5 million or about \$1250 per metric ton. It is important to decrease both the amount of hazardous waste generated and the cost of disposal per ton.

DESCOM Hazardous Paint Blast Media Wastes

Unlike most AMC waste streams, hazardous paint blast media waste is actually increasing. One reason for this is that abrasive depaint methods are replacing chemical strippers for many applications. Another factor is the change in analytical methods used for determining whether paint blast media wastes are hazardous. The EP Tox test has been supplanted by the more rigorous toxic characteristic leaching procedure (TCLP). Some waste streams which passed under the old test method fail to pass the TCLP. Wastes which are identified as hazardous may contain one or more metals. Typical hazardous constituents are lead, cadmium, and chromium.

A wide variety of abrasive blast media types are used at DESCOM facilities including mineral abrasives, plastics, agricultural products, ceramic materials, and metals. Many of these media may be classified as durable abrasives. Durable abrasives such as plastic media and steel grit may be recycled many times. This reduces total waste generation but concentrates contaminants in the

spent media. Concentrating the contaminants increases the likelihood that a hazardous waste will be generated. However, the overall economics still favors the use of durable abrasives. The materials cost of expendable abrasives, their higher handling costs and the larger volumes requiring disposal, will in most cases outweigh cost savings derived from classification of the wastes as nonhazardous. This also assumes that these more dilute wastes would in fact be classified as nonhazardous. Indeed, experience derived in the maintenance painting industry with bridges has shown that many expendable once-through abrasives are classified as hazardous.

Approaches to Paint Blast Media Waste Hazmin

Waste reduction is always the first approach which should be considered when examining a hazardous waste generation problem. Process related reductions have for the most part been maximized in DESCOM facilities through the use of durable recyclable abrasives. Reductions through process avoidance is a possible avenue to significant reductions. This could be accomplished by extending the maintenance cycle for some systems or components. Future hazardous wastes could be greatly reduced by replacing chromium, cadmium, and lead compounds in depot plating and painting processes.

Waste treatment methods may be used to compliment process Waste treatment methods based on oriented waste reduction. separation of the spent blast media fines from the hazardous paint chips has been suggested as a means of reducing the volume of hazardous waste. A separation efficiency of 100-percent could translate to waste reductions of 90-percent or higher. separation, although at first quite attractive, may not be practical at DESCOM facilities, since a wide range of blast media are employed. Separations based on density differences between the spent media and paint residue are feasible. Plastic and agricultural media have relatively low densities while mineral and metallic abrasives are much more dense. Density separation techniques would have to be engineered to suit individual waste streams. This could possibly require separate process units for multiple waste streams at depot facilities. Spent blast media and paint wastes may in some cases have very similar densities making separation difficult. Density separations affected by settlement in an aqueous solution may result in contamination of the liquid phase thus generating a new hazardous waste. Separation technologies would probably have relatively high operating and capital costs. Alternatively, the waste treatment industry has developed a wide variety of relatively inexpensive waste treatment techniques which may be more cost effective than waste separation.



Hazardous Waste Solidification/Stabilization

Resource Conservation and Recovery Act (RCRA) hazardous wastes such as lead, cadmium, and chromium contaminated paint blast media, are subject to Land Disposal Restrictions (LDRs). established in recognition of the probable fate of contaminated wastes disposed of in or on the land. As a result of the LDRs the Environmental Protection Agency (USEPA) has established treatment standards for RCRA hazardous wastes. Treatment standards are based on Best Demonstrated Available Technology (BDAT). BDATs may be specified as either waste specific treatment technologies or as post treatment concentration limits. Abrasive blasting wastes typically are classified as hazardous for the presence of one or more DO4-DO11 metals. The BDAT for blast wastes contaminated with lead, cadmium, and chromium are concentration based. The treatment standard for lead containing waste is 5 ppm as determined by TCLP. Any treatment technology which reduces the leachable lead content to below 5 ppm is acceptable.

Solidification/stabilization procedures may be used to process hazardous wastes into non-hazardous wastes. Stable binders such as Portland cement may be used to solidify the waste material. The physical binding which occurs during solidification may include absorption, adsorption, or encapsulation. The solidified wastes are less permeable to water and thus have reduced leach rates of hazardous constituents. Stabilization refers to a chemical interaction between the waste and treatment material. Stabilized wastes are less chemically active and therefor less susceptible to leaching.

The primary advantage of solidification/stabilization waste treatment processes is the ready availability and low cost of the treatment materials. Equipment and processing costs are also low. Solidification/stabilization is suggested for treatment of metal contaminated wastes such as hazardous paint blast media wastes. The main disadvantage of solidification/stabilization is that the treatment results in a greater volume of waste which must be disposed.

Prior to fully implementing a waste treatment technology it is advisable to thoroughly evaluate the process by conducting a treatability study. Treatability studies are being conducted on DESCOM paint blast media wastes to determine compliance with regulatory requirements, long-term environmental fate, and cost.

Table I identifies the waste streams which are being evaluated in the study. Each waste stream is being tested for DO4 through DO11 metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver) using TCLP. Hazardous waste streams are stabilized by mixing with 10-percent and 20-percent by volume ASTM C150 Portland Cement. Stabilized wastes are being re-evaluated for toxic leachates with TCLP. Bulk densities are measured before and after treatment with Portland cement and the weight percent of cement in each sample calculated. This information will be used to

help predict weight based disposal costs and cement costs.

Additional research will be conducted to evaluate the mechanism of Portland cement stabilization. A systematic study of synthetic cement pore composition will be performed. Typical ASTM Type I and atypical high-alkali cements will be utilized. The ratio of model pore solution to blast media waste will be varied from 0.2 to 50. Leachate analyses will be determined over a 28-day period using inductively coupled plasma-atomic emission spectroscopy. These experiments should also be of value in predicting the long-term waste stability under high pH conditions which are associated with Portland cement.

Table I.

DESCOM Facility	Waste Stream
Anniston Army Depot	glass beads steel shot Black Beauty™ Green Lightening™ walnut shells aluminum oxide
Corpus Christi Army Depot	plastic media Starbrite™
Letterkenny Army Depot	walnut shells steel shot plastic media glass beads plastic and glass
Red River Army Depot	sand garnet stainless steel steel shot walnut shells plastic media glass beads
Sacramento Army Depot	plastic media garnet and sand glass beads

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SMALL IMPOUNDMENT FISHERIES-A RECREATIONAL OPPORTUNITY FOR MILITARY INSTALLATIONS

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ABSTRACT

Military installations have hundreds of small impoundments (< 500 surface acres) but many are underutilized by anglers because of a lack of systematic management. These aquatic habitats, with management, are capable of supporting much greater fishing effort and harvest than warmwater rivers and reservoirs. Small impoundments are ecologically unstable and hence are readily managed. Sustained yearly harvest of several hundred pounds of fish per acre and hundreds of hours of fishing for each surface acre are possible. Management considerations include impoundment design, stocking, fertilization, population assessment, and regulating harvest to achieve sustainable fisheries. The fish community is easily evaluated by seining or electrofishing during the summer. A comprehensive program to evaluate the management potential of these impoundments and establish recreational fisheries is consistent with environmental and stewardship goals of the Department of Defense.

INTRODUCTION

Small impoundments are an underdeveloped recreational fisheries resource on many military reservations. Many impoundments constructed on military installations were built for short-term use, such as training sites or for erosion control, and were then neglected. Unmanaged impoundments often become increasingly shallow due to sedimentation, are populated by nuisance levels of vegetation, and have unbalanced fish populatons. A review of the literature suggests natural systems have a tenth to a fifth the harvest potential of a well managed small impoundment (Jenkins and Morais 1971). Proper management of these systems could provide angling opportunities to military personnel and conserve aquatic habitat.

Two separate disciplines must be employed to fully utilize this resource: fisheries management and engineering. Engineering assistance is important to 1) ensure safety and 2) design the impoundment to allow full achievement of the fisheries potential. In this article we discuss how small impoundment fisheries function and describe management techniques.

MANAGEMENT OF BALANCED IMPOUNDMENTS

The goal of small impoundment management is to achieve "balance" which means yearly production of harvestable fish in proportion to the productivity of the impoundment (Swingle 1950). Balanced fish communities are defined biologically by ratios such as harvestable to nonharvestable fish, carnivorous to forage species, and the percent by weight

of each species relative to the entire fish community. These ratios have acceptable ranges for balance and are termed community biomass ratios (Table 1). To achieve balance the following conditions must be met: 1) proper design of the impoundment, 2) stocking the right species in the proper numbers, 3) achieving a satisfactory level of productivity, 4) controlling competing species, 5) performing yearly assessment to insure balance is maintained, and 6) imposing appropriate harvest restrictions (Swingle 1950, 1956; Davies 1974). Balanced small impoundments can be productive: a yearly harvest of several hundred pounds per acre is possible in the southern and midwestern U. S.

Design and Construction

Engineering should focus on two components: safety of the impoundment and design features that enhance the recreational fishery potential. Safety features should be evaluated by a competent engineer and include water budgets, dike construction, and design of water control structures. Failure to consider dam safety endangers people living downstream, can be a source of litigation, and can cause unnecessary and expensive repairs. Engineering also affects the fishery potential. Properly matching the watershed to the impoundment is necessary to establish water budgets that favor raising fish, controlling aquatic vegetation, and maintaining stable water levels (Lawrence 1949). For example, too much water flowing into a pond will flush out nutrients negating an effective fertilization program. The impoundment should also be designed to prevent emigration of fish from the surrounding watershed; non-stocked species can compete for food and space with stocked species. This means not building an impoundment on a major stream and having sufficient barriers to prevent fish from entering. Usually, a two foot drop of outflow is sufficient. The final design factor is to have the edges deepened to approximately 18 to 24 inches to prevent establishment of rooted plants.

Fertilization

A nutrient enhancement program using a high phosphorus fertilizer is usually necessary to raise the carrying capacity of the impoundment (Swingle 1950; Boyd 1973, 1976, Dobbins and Boyd 1976). This practice is common in the southern and western parts of the country but should be avoided in colder climates where winter oxygen depletions can occur under ice. The first step in a fertilization program is to lime the impoundment as necessary (Boyd 1976) and then fertilize using a high phosphorus fertilizer such as triple superphosphate (0-46-0) until a green "bloom" of microscopic algae is established that limits visibility in the water column to approximately 18 to 24 inches. This bloom substantially increases the carrying capacity for the fish community and shades out rooted aquatic plants (Boyd 1975). Never fertilize if aquatic plants have become established, instead eradicate the plants and then start a fertilization program. In impoundments where fertilization is not feasible, a program of using pelleted fish feeds may raise the carrying capacity of the impoundment. The daily feeding rate should be approximately 1 to 3 percent of the estimated weight of the standing crop of bream (sunfishes).

Stocking

Fisheries management begins by stocking the appropriate numbers of fish and the right species. Stocking techniques have been developed for warmwater impoundments in the southeastern and midwestern United States and apply, with modification of species and numbers, in other regions (Dillard and Novinger 1975). A mixture of sunfish fingerlings, called bream, should be stocked in the late fall or early winter months. The usual mixture is 75% bluegill Lepomis macrochirus and 25% redear sunfish Lepomis microlophus at a rate



of 1000 fingerlings per acre. If the impoundment is not to be fertilized, one half the stocking rate should be used. In May to June, fingerling largemouth bass Micropterus salmoides should be stocked at a rate of 100 per surface acre; use one half the rate in unfertilized systems. No fish should be present in the impoundment when fingerlings are stocked since any predation or competition for food will affect stocking ratios. There may be times, especially in larger impoundments, when other species such as crappie (Pomoxis spp.) and catfishes (Ictalurus spp.) become established. Their establishment makes management more problematical and requires more sophisticated management strategies (Swingle 1956; Davies 1974). Establishment of short food chain species such as shad (Dorosoma spp.) should be avoided since competition with balanced fish communities is probable (Kirk et al. 1986; Kirk and Davies 1986).

Monitoring

Small impoundments should be ready for fishing about two years after stocking. Good records should be kept, especially of the largemouth bass harvest. Summertime seine analysis, called balance checks, should begin the second summer after stocking. Balance checks use a 15 and 50 foot seines to determine the state of balance by examining small fishes easily captured by the seines. A 15 foot seine is used to determine if both largemouth bass and bluegill have spawned successfully. The 50 foot seine is used to collect bream in the 3 to 5 inch size range called intermediates. By knowing this information, a biologist can tell whether or not the impoundment is in balance and how many bass or bluegill can be harvested during the remainder of the year. Seine analysis can often detect the presence of competing species, problems in establishing adequate productivity, and under or over harvest of largemouth bass (Swingle 1956). Similar types of balance assessment have been developed for midwestern small impoundments by Anderson (1978) using electrofishing and weight to length information.

IMPORTANCE IN THE FUTURE

Small impoundments offer an underutilized and very productive source of angling. Current surveys indicate that freshwater angling is a significant form of recreation that is likely to grow in importance in the future (USFWS 1989). Small impoundment fisheries are often close to home and require no specialized fishing gear. Further, well managed small impoundments provide greater harvest potential than most natural systems. Many existing small impoundments on military installations could be renovated and made productive, while new impoundments could be constructed for a reasonable cost. All impoundments should regularly be evaluated for safety. Biologists and engineers should work together on the design, suitability and safety of small impoundments as well as all areas of fisheries management.

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Table 1. Community biomass ratios for balanced fish populations in small impoundments (Swingle 1950).

Biomass ratio	Optimum range	
Forage to carnivorous species (F\C)	3-6	
Percentage of the total weight of harvestable fish (AT)	60-85	
Percentage weight of the entire	Bluegill 66-85	
population of a species or group	Largemouth bass 33-15	

A COMPREHENSIVE NUMERICAL MODEL FOR SIMULATING THE FLOW OF PETROLEUM PRODUCTS AND INDUSTRIAL CHEMICALS IN THE SUBSURFACE

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INTRODUCTION

The release and subsurface migration of non-aqueous phase liquids (NAPL such as oily wastes, petroleum products and industrial chemicals) have caused serious groundwater contamination problems nationwide. Modeling assessments of contaminant migration and remedial options are becoming crucial due to the increased necessity to address and mitigate the environmental problems. Numerous models are available for single-phase simulation of groundwater flow and contaminant transport. Multiphase NAPL migration modeling, however, is still faced with two major challenges. First, significance of key processes and assumptions of the governing equations need to be evaluated. Second, robust numerical techniques are essential to overcome mass balance and convergence difficulties and excessive computational burden arising from highly nonlinear fluid retention characteristics and large heterogeneities encountered in field simulations.

Although a fair number of numerical models of various levels of sophistication have been developed for simulating water flow and NAPL migration in subsurface systems, there are very few reported studies of the practical application of these models for assessing full-scale pollution sites, or for examining alternative remediation strategies. Existing models are not commonly applied to site-specific problems for several reasons. First of all, the available models are generally too computationally intensive to apply to typical field-scale problems. This stems from the fact that the system of equations describing the multiphase flow of NAPL, water and air in the subsurface is often extremely non-linear and difficult to solve. Secondly, most of the existing models do not include all of the relevant physics e.g., neglecting air-phase dynamics. Thirdly, some of the well publicized models (e.g., Faust, 1985; Faust et al., 1989; Kaluarachchi et al., 1990; and Kaluarachchi and Parker, 1989) have a number of additional limitations. For example the numerical solution schemes presented by Faust (1895) and Faust et al. (1989) can not handle certain combinations of practical boundary conditions (e.g., specification of two liquid-phase pressures). The models presented by Kaluarachchi and Parker (1989) and Kaluarachchi et al. (1990) suffer large mass balance error and convergence difficulties. Finally, the existing models are, in general, too complex to be successfully applied by hydrogeologists and other professionals that have not undergone intensive special training. Due to these difficulties, even though various models have been developed for simulating multiphase flow systems, few studies have been performed that utilize these models for examining alternative site remediation strategies.

This study describes a comprehensive model designed to overcome the shortcomings of previous modeling efforts for NAPL flow. First, a rigorous three-phase model formulation for the most general case of all fluid phases flowing within a porous medium is discussed. The flow

formulation collapses to its simpler forms (applied in most current NAPL migration models) in which the air-phase dynamics are neglected (passive air-phase assumption). Further simplifications may be achieved when capillary effects are neglected, or when two-phase air-liquid, liquid-liquid systems with one or two active phases are considered.

In addition, a sharp-interface vertical-equilibrium (VE) approach (Coats et al., 1967) is also incorporated. The VE model can be obtained from the multiphase model when liquid-phase pressures are approximately hydrostatic. The VE approach has the following advantages over the more rigorous multiphase model. Problem dimensions are reduced by one, i.e., 3-D and 2-D (cross sectional) problems become 2-D (areal) and 1-D problems, respectively. Hence, savings in computational resources can be substantial. Input data requirements for relative permeability and capillary pressure are removed by using a sharp-interface assumption. Therefore, the sharp-interface VE approach is suitable for preliminary evaluations at sites where data availability is limited.

Several VE numerical models have recently been proposed for areal simulation of NAPL migration (Hochmuth and Sunada, 1985 and Parker and Lenhard, 1989). However, these models can only handle lighter-than-water, but not denser-than-water NAPL. Furthermore, there are other shortcomings in the model formulations. In the model of Parker and Lenhard a hydrostatic condition is assumed not only in liquid-saturated zones but also in unsaturated zones. A hydrostatic condition implies that flow is strictly is the horizontal direction, but the flow in unsaturated zones is predominantly in the vertical direction. The model of Hochmuth and Sunada incorporates the residual saturation in the storage terms of the equations. However, the effects of the storage terms vanish when steady-state conditions are reached. Therefore, situations where the NAPL mass becomes immobile at residual saturation cannot be predicted. The VE model presented in this study overcomes the shortcomings.

Robust and efficient numerical techniques have been incorporated in our proposed VE model to enable practical simulations of site-specific field problems on PC's and workstations. The governing equations are discretized using a modified Galerkin finite element method with an influence coefficient scheme for element matrix computation thereby avoiding costly numerical integration. Nonlinearities are treated using the Newton-Raphson technique. The convergence and efficiency of the overall nonlinear solution procedure are enhanced by an advanced time stepping control scheme which takes the full advantage of the Newton-Raphson scheme. The resulting set of linear algebraic equations is solved by the ORTHOMIN accelerated matrix iterative method (Behie and Forsyth, 1984).

Simulation examples are presented that depict the migration of lighter-than-water and denser-than-water NAPLs (LNAPL and DNAPL). The significance of the sharp-interface VE modeling approach is examined in view of modeling and data requirements and reliability of simulation results. The strength of the numerical schemes is also demonstrated with the simulation examples. The present model provides an effective tool for prediction of the NAPL migration and evaluation of remedial designs.

MODEL DESCRIPTION

The governing equations for a multiphase flow system are readily available in the literature. Therefore, they are introduced without derivation. The governing equations for the VE approach are similar to those presented by Coats et al. (1967). However, the assumptions and procedures used are different from those in the more recent vertically integrated models (Hochmuth and Sunada, 1985 and Parker and Lenhard, 1989). Therefore, a brief description is given on the derivation.

Although the governing equations for the multiphase and the VE approaches are different, there are enough common characteristics so that the same numerical approximation and solution strategy can be used for both approaches. A modified Galerkin finite element method was used for discretization, and the Newton-Raphson scheme was used for nonlinearities.

Multiphase Flow Model

The standard multiphase flow equations may be written in the form (Thomas, 1982):

$$\frac{\partial}{\partial x_i} \left[k_{ij} \tau_{\ell} \frac{\partial \Phi_{\ell}}{\partial x_j} \right] = \frac{\partial}{\partial t} (\phi \rho_{\ell} S_{\ell}) - \Gamma_{\ell} , \ell = w, n, g$$
 (1)

where k_{ij} is the intrinsic permeability tensor, τ_{ℓ} is the phase mobility ($\tau_{\ell} = k_{r\ell} \rho_{\ell}/\mu_{\ell}$, in which $k_{r\ell}$ = relative permeability, and μ_{ℓ} = dynamic viscosity), Φ_{ℓ} is the fluid potential ($\Phi_{\ell} = p_{\ell} + \rho_{\ell}gz$, in which p_{ℓ} = phase pressure, ρ_{ℓ} = phase density, g = gravitational constant, and z = elevation above the datum), ϕ = porosity, S_{ℓ} = phase saturation, and Γ_{ℓ} = source/sink.

The flow equations (1) need to be supplemented by the following constitutive relations (Forsyth and Shao, 1991):

$$S_w + S_n + S_g = 1 \tag{2}$$

$$p_{g} = p_{n} + \alpha p_{cgn}(S_{g}) + (1 - \alpha) \left[p_{cgw}(S_{g}) - p_{cnw}(S_{w} = 1) \right]$$
 (3)

$$p_n = p_w + \alpha p_{cnw}(S_w) + (1 - \alpha) p_{cnw}(S_w = 1)$$
 (4)

$$k_{r\ell} = k_{r\ell}(S_w, S_g) \qquad , \ell = w, n, g \tag{5}$$

where p_{cgw} , p_{cnw} and p_{cgn} are capillary pressures for the three fluid pairs (gas, water), (NAPL, water) and (gas, NAPL), respectively, and α is the fluid interface transition parameter defined as $\alpha = \min (1, S_n/S_n^*)$ with S_n^* being the NAPL threshold saturation below which NAPL cease

to exist as a continuously connected phase, and hence some air is directly in contact with the water phase.

In general, the relative permeability and the capillary pressure are functions of saturation. To provide flexibility to our proposed model, relative permeability and capillary pressure data may be provided in functional or tabular forms. With the functional option, we allow the use of either the Brooks and Corey (1966) or the van Genuchten (1980) extended relative permeability functions for the three-phase fluid system. Capillary pressure functions adopted correspond to the scaled functions presented by Lenhard and Parker (1987). With the tabular option, the three-phase NAPL relative permeability may be calculated using the first or second method of Stone (1970, 1973). In addition to the above constitutive relations, equations of state are needed to determine fluid densities and medium porosity as functions of pressures.

Vertical Equilibrium Model

For liquid saturated zone the gas phase vanishes, and the flow system becomes two phase (water and NAPL). The two-phase flow system is considered to be in vertical equilibrium (VE) whenever the pressure in each liquid phase is approximately hydrostatic. Conditions of VE are satisfied in aquifers having one or more of the following properties (Thomas, 1982):

- (a) high vertical permeabilities,
- (b) high gravity and/or capillary zones,
- (c) high fluid mobilities,
- (d) low rates of areal fluid movement, and
- (e) low vertical potential gradients.

When the VE approximation is applicable, the dimension of the two-phase flow system can be reduced by one by integrating equations along the vertical direction over the liquid saturated thickness. The integrated equations are further simplified using the Leibnitz's rule and for unconfined aquifers, the free liquid-surface condition (Bear, 1972) at the liquid-air interface. Then, the governing equations under the VE approximation for a homogeneous aquifer with a constant saturated thickness become

$$\frac{\partial}{\partial x} \left[\frac{\rho_{\ell} b}{\mu_{\ell}} k_{x} \overline{k}_{r\ell x} \frac{\partial \Phi_{\ell}}{\partial x} \right] + \frac{\partial}{\partial y} \left[\frac{\rho_{\ell} b}{\mu_{\ell}} k_{y} \overline{k}_{r\ell y} \frac{\partial \Phi_{\ell}}{\partial y} \right] = \frac{\partial}{\partial t} \left(\rho_{\ell} b \phi \overline{S}_{\ell} \right), \quad \ell = w, n \quad (6)$$

where b is the thickness of liquid saturated zone, and the vertically averaged variables are defined as

$$\overline{k}_{r\ell} = \frac{1}{b} \int_{Z_B}^{Z_T} k_{r\ell}(z) dz$$
 (7)

and

$$\overline{S}_{\ell} = \frac{1}{b} \int_{Z_B}^{Z_T} S_{\ell}(z) dz$$
 (8)

where Z_B is the aquifer base elevation, and Z_T is the top elevation of the liquid saturated zone, which, in general, is a function of both space and time. In addition to the average relative permeability a pseudo capillary pressure relation is needed to relate different phase pressures.

In general, the dependence of the average relative permeability and the pseudo capillary pressure on the average saturation can be determined using real capillary pressure and relative permeability curves at the reference plane and the VE condition (Coats et al., 1967, Martin, 1968). However, computational efforts involved in generating the pseudo functions using the real soil properties may be extensive. One of simplifications in constructing the pseudo functions is to ignore the capillary transition zone by assuming that a sharp-interface separates the zones of NAPL and fresh water. Such a condition is referred to gravity-segregated vertical equilibrium (Coats et al., 1971, and Thomas, 1982). In our model this sharp-interface approach is incorporated.

Numerical Techniques

We propose the development of a comprehensive numerical model with efficient and robust numerical techniques suitable for handling complex field problems. The proposed model is comprehensive in the sense that it can perform rigorous multiphase analyses for cross-sectional problems and efficient VE analyses for areal problems, and can handle LNAPL and DNAPL. In this section a brief description of the numerical scheme is given for the three-phase model. The procedure for the two-phase VE model is analogous.

A flexible modified Galerkin finite element scheme was devised. The scheme incorporates upstream weighting of phase mobilities and storage matrix lumping (Huyakorn et al., 1991). The time derivative is approximated using a fully implicit time integration. Then, the discretized equations become

$$\sum_{J \in \eta_{I}} \tau_{\ell IJ}^{u} \gamma_{IJ} \left(\Phi_{\ell I} - \Phi_{\ell J} \right)^{t + \Delta t} + \frac{B_{I}}{\Delta t} \left[\left(\phi \rho_{\ell} S_{\ell} \right)_{I}^{t + \Delta t} - \left(\phi \rho_{\ell} S_{\ell} \right)_{I}^{t} \right] = M_{\ell I}^{\bullet}$$

$$\ell = w, n, g \qquad I = 1, 2, ..., n$$
(9)

where η_I is the set of neighboring nodes connected to node I, $\tau_{\ell IJ}^u$ is the upstream value of mobility associated with flow of phase ℓ , γ_{IJ} are transmissivity coefficients that may be readily computed using newly developed influence coefficient algorithms thereby avoiding numerical integration, B_I is the nodal volume, $\dot{M}_{\ell I}$ is the sink/source term introduced to account for boundary conditions, and n is the total number of nodes in the grid.

The nonlinearity in (9) is handled using a residual-based, Newton-Raphson iterative technique. To obtain optimal behavior of the numerical solution in terms of convergence and mass balance, the primary variables must be carefully selected. For the three-phase flow situation, we select p_g , S_n and S_g as the three primary variables, and for the VE flow situation we select a pressure and a saturation as the two primary variables depending on the type of NAPL. Equation (9) is rewritten in the following form:

$$R_I^{\ell}(p_{gI}, S_{nI}, S_{gI}) = 0, I = 1, 2, ..., n$$
 (10)

Application of the Newton-Raphson procedure to (10) yields

$$\frac{\partial R_I^{\ell}}{\partial p_{gJ}} \Delta p_{aJ} + \frac{\partial R_I^{\ell}}{\partial S_{nJ}} \Delta S_{nJ} + \frac{\partial R_I^{\ell}}{\partial S_{gJ}} \Delta S_{gJ} = -(R_I^{\ell})^k$$
 (11)

where k is the iteration level and, for each primary variable χ , the increment value is defined as $\Delta \chi = \chi^{k+1} - \chi^k$. When applied to all nodes, (11) becomes a system of linear equations. Since the coefficient matrix for a typical problem is large and sparse, the matrix equation needs to be handled using an efficient iterative matrix solver. The iterative algorithm using an incomplete factorization with the ORTHOMIN acceleration presented by Behie and Forsyth (1984) was selected. A sparse matrix storage is used to minimize computer storage requirements thus allowing the proposed models to accommodate realistic field problems with several hundred thousand nodes on a work station or minicomputer.

The convergence and efficiency of the overall solution procedure are enhanced by the combined use of automatic under-relaxation and aggressive time stepping schemes. The automatic time stepping procedure used is simple but aggressive. The initial time step size Δt_1 is chosen by the user. If the nonlinear solution converges in less than a specified number of iterations, the next time step size is automatically increased. If the convergence is not obtained within an allowable nonlinear iterations, the time step is automatically reduced. The factor of increase or reduction of the time step size can be as large as 5 and is determined based on the rate of convergence in the previous time step. This time stepping procedure works very well with our Newton-Raphson mixed formulation but would be far too aggressive for the Picard-

based pressure head formulations such as those of Reeves and Abriola (1988), and Kaluarachchi and Parker (1989), where on page 47 their time multiplier F is limited to only 1.04 or less to avoid convergence difficulties.

MODEL VERIFICATION AND SIMULATION EXAMPLES

Verification of the three-phase model was reported by Huyakorn et al. (1991). Several analytical solutions of Buckley-Leverett type problems and other numerical modeling results (Forsyth and Shao, 1991 and Faust, 1985) were used. Good agreement with the results of our three-phase model was observed. Although simulation examples of the three-phase model were made on two-dimensional cross-sectional problems, the governing equations and the numerical techniques previously described are readily applicable to three-dimensional problems. Three-dimensional applications of the three-phase model are subject of a forthcoming paper. In the present paper we elect to present four simulation examples that demonstrate the verification and application of the VE modeling approach. In the first two example comparisons are presented with the solutions of the multiphase flow, for LNAPL and DNAPL. The third example demonstrates the capability of the VE approach with nonzero NAPL residual saturation. The final example involves three-dimensional NAPL lenses evolved from two sources. The solution was obtained using the VE approach.

Example 1. Comparison of the VE Model with the Multiphase Model for LNAPL Flow

The simulated flow domain is similar to that used by Faust (1985), however, we changed the bottom and right-hand side boundary conditions to consider horizontal groundwater flow. As shown in Figure 1(a), the flow system consists of a surficial unit of 5 m thick and is subject to a uniform infiltration rate of 0.1 m/y (100 kg/y/m²). The NAPL source is located at the center of the domain and its leakage rate was assumed to be 1800 kg/y. Since the flow domain is symmetrical, only one half was modeled. No flow boundary conditions were applied at the symmetry line and at the aquifer bottom. Prescribed constant potentials were used at the saturated portions of the side boundaries.

A summary of physical parameter values used in the simulation is provided in Table 1. Shown in Table 2 is the relative permeability data which correspond to that used by Faust (1985). The capillary pressure effects were considered to be insignificant and were ignored in the multiphase modeling. In the sharp-interface VE simulation, the residual saturation of LNAPL was set to zero. A 13 x 21 cross-sectional grid of uniform spacing was used for the multiphase model. A 13 x 2 areal grid was used for the 1-D VE modeling. Although the example is one-dimensional for the VE model, a two-dimensional areal grid was used for the simulation.

Comparisons of the LNAPL lenses at two time values of 338 and 696 days, predicted by the three-phase and the sharp-interface VE models are given in Figures 1(b) and (c), respectively. Also presented in the Figures are vertical saturation distributions below the source obtained using the three-phase modeling option. The agreement between the two approaches is

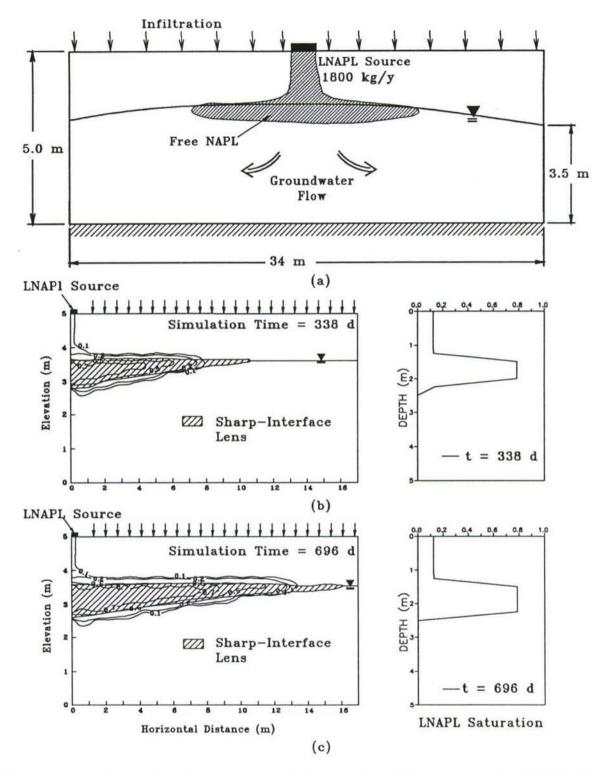


Figure 1 Comparison between the multiphase and the VE approaches for LNAPL flow (a) schematic diagram, results at (b) 338 days and (c) 696 days.



Table 1 Physical parameter values used in the analysis of Examples 1 and 2.

Parameter	Value
Intrinsic Permeability	1 x 10 ⁻¹² m ²
Porosity	0.3
Water Density	$1,000 \text{ kg/m}^3$
LNAPL Density	950 kg/m^3
Water Viscosity, μ_{w}	1 x 10 ⁻³ Pa.s
LNAPL Viscosity, μ_n	1 x 10 ⁻³ Pa.s
Water Infiltration Mass Flux	100 kg/y/m^2
Total LNAPL Injection Rate	900 kg/y

Table 2. Relative permeability data used in the analysis of Examples 1 and 2.

V	Vater-NAPL Data		
$S_{\mathbf{w}}$	k _{rw}	k _{rn} ^{wn}	
0.2000E+00	0.0000E+00	0.6800E+00	
0.3000E + 00	0.4000E-01	0.5500E+00	
0.4000E + 00	0.1000E+00	0.4300E+00	
0.5000E+00	0.1800E+00	0.3100E+00	
0.6000E+00	0.3000E+00	0.2000E+00	
0.7000E + 00	0.4400E+00	0.1200E+00	
0.8000E + 00	0.6000E+00	0.5000E-01	
0.9000E+00	0.8000E + 00	0.0000E+00	
0.1000E+01	0.1000E+01	0.0000E+00	
1	NAPL - Air Data		
Sa	k _{ra}	$\mathbf{k_{rn}^{na}}$	
0.0000E+00	0.0000E+00	0.6800E+00	
0.6800E + 00	0.6800E+00	0.0000E+00	
0.8000E+00	0.8000E + 00	0.0000E+00	
	S _w 0.2000E+00 0.3000E+00 0.4000E+00 0.5000E+00 0.6000E+00 0.7000E+00 0.8000E+00 0.9000E+01 S _a 0.0000E+00 0.6800E+00	0.2000E+00	Sw krw kmn 0.2000E+00 0.0000E+00 0.6800E+00 0.3000E+00 0.4000E+01 0.5500E+00 0.4000E+00 0.1000E+00 0.4300E+00 0.5000E+00 0.1800E+00 0.3100E+00 0.6000E+00 0.3000E+00 0.2000E+00 0.7000E+00 0.4400E+00 0.1200E+00 0.8000E+00 0.6000E+00 0.5000E-01 0.9000E+00 0.8000E+00 0.0000E+00 0.1000E+01 0.1000E+01 0.0000E+00 NAPL - Air Data kra kna NAPL - Air Data kra kna 0.0000E+00 0.6800E+00 0.6800E+00 0.6800E+00 0.6800E+00 0.0000E+00

reasonable. However, the NAPL lens produced by the three-phase approach is bigger than the one by the VE approach because the former contains water inside (i.e., $S_{\rm n} < 1$).

The most obvious advantage of the VE approach due to the reduction in problem dimensions appears in computer simulation times. For 696-day results the three-phase approach

took 10 minutes on a MIPS workstation while the VE approach took less than 1 minute on a 25 MHz 386 PC. The MIPS workstation is 5 to 10 times faster than the PC.

Case 2. Comparison of the VE Model with the Multiphase Model for DNAPL Flow.

This example involves DNAPL flow in an aquifer with a tilt bottom (Figure 2(a)). The density of DNAPL used in the simulation was 1200 kg/m³, and all the other parameters and relative permeability curves were the same as those in the LNAPL case, given in Tables 1 and 2. An irregular grid of 13 x 21 was selected for the cross-section in the multiphase simulation. The same 1-D grid as in Example 1 was used for the 1-D VE model.

Two simulations were made using the three-phase modeling option to examine the DNAPL saturation distributions directly beneath the source, with and without the influence of capillarity. Figure 2(b) shows the vertical distribution of DNAPL saturation from the source without capillary pressure effects. Figure 2(c) shows the saturation distribution with strong capillary effects. The capillary pressure data used is given in Table 3. Both results indicate that the movement of DNAPL is predominantly vertical and the saturation is slightly higher than the residual saturation. Furthermore, sensitivity analyses using a rigorous multiphase model (Huyakorn et al, 1991) indicated that DNAPL tends to move straight down from the source until it reaches the aquifer bottom. Therefore, for the VE model the column of NAPL at residual saturation (Figure 3(d)) was allowed to form in the following manner. First, the storage capacity of the aquifer beneath the source due to the residual saturation is computed. Then, the first part of NAPL release at the source would be used to fill the residual storage column, and the simulation of NAPL flow by the VE model would start only after the cumulative amount of the NAPL release at the source exceeds the residual storage capacity.

A comparison of DNAPL lenses predicted using the three-phase and the VE modeling approaches is shown in Figure 2(d) when the capillary pressure effects were ignored. The agreement between the two NAPL lenses at the aquifer bottom is reasonable. The CPU times spent by the two models compare similarly with those of the previous LNAPL example.

Example 3. 1-D VE Model Results for LNAPL and DNAPL with Residual Saturation

The simulated aquifer system is depicted in Figure 3(a). The cross section is 2000 meter long and 25 meter thick. The bottom boundary is assumed to be impermeable. The top boundary is subject to the uniform infiltration rate of 5 cm/y. The NAPL source is 50 meter long and releases NAPL at the rate of 1000 kg/y/m² for a year. The flow domain was approximated using a non-uniform mesh consisting of 13 rectangular elements and 28 nodes. Physical parameters of fluids and formation used in the simulation are listed in Table 4.

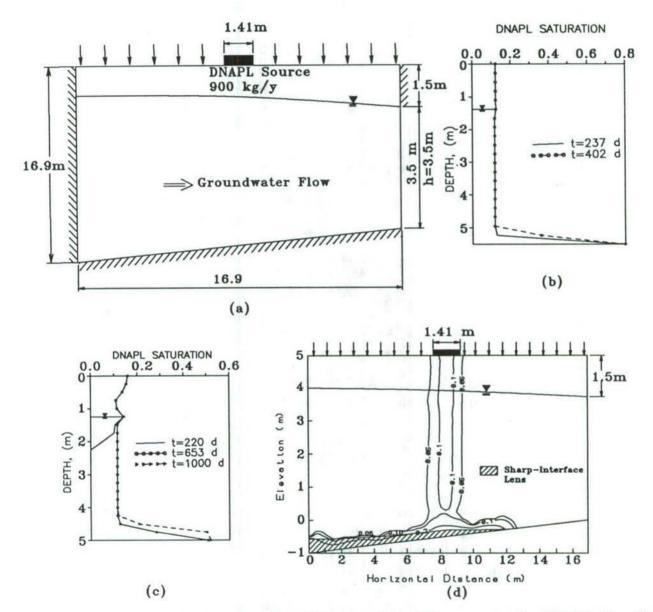


Figure 2. Comparison between the multiphase and the VE approaches for DNAPL flow (a) schematic diagram, (b) saturation profile without capillary effects, (c) saturation profile with capillary effects and (d) saturation distributions by the two approaches at 402 days.

Table 3. Capillary pressure date used in the analysis of Example 2.

Two-Phase Wa	Two-Phase Water-NAPL System					
$S_{\mathbf{w}}$	P _{cnw} (Pa)					
0.2000E+00	0.1034E+06					
0.3000E + 00	0.2758E+05					
0.4000E + 00	0.1034E+05					
0.5000E + 00	0.7585E+04					
0.6000E + 00	0.7447E+04					
0.7000E + 00	0.7309E+04					
0.8000E + 00	0.7171E+04					
0.9000E+00	0.7033E+04					
0.1000E+01	0.6895E+04					

Liquid - Air Data

S_a	P _{can} (Pa)	P _{caw} (Pa)	
0.0000E+00	0.0000E+00	0.6895E+04	-
0.6800E + 00	0.6664E + 05	0.8388E+05	
0.8000E + 00	0.7710E+05	0.1805E + 06	
	0.0000E+00 0.6800E+00	0.0000E+00	0.0000E+00

(a) LNAPL Case

The VE model simulation results for LNAPL movement are presented in Figures 3(b) and (c) at two different times, 11 and 58 years, respectively. As it can be seen from Figure 3(b) there are two distinct zones of LNAPL, mobile and immobile. At a much later time after the termination of NAPL recharge, all NAPL mass is captured by residual saturation and the lens becomes immobile. This situation is depicted in Figure 3(c).

(b) DNAPL Case

In this case the NAPL source release DNAPL while the rest of the conditions remain identical as in the previous case. The simulated plumes are shown in Figures 3(d) and (e) at two time values of 8 and 41 years, respectively. As expected, the DNAPL mass accumulates on the bottom of the aquifer and is transported by the ambient groundwater. As was in the LNAPL case, the mobile NAPL mass leaves behind the immobile mass captured by the residual saturation. The column of NAPL residual saturation below the source was obtained using the approach previously described.

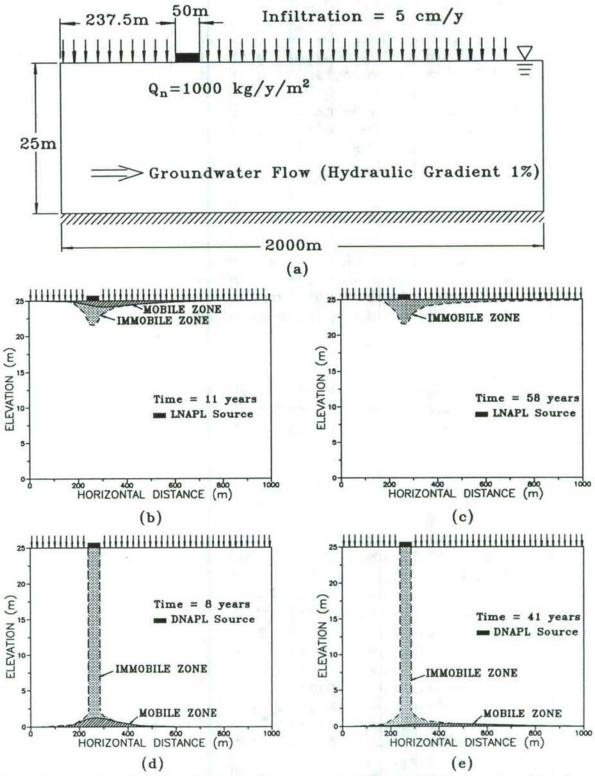


Figure 3 One-dimensional NAPL flow example with residual saturation (a) schematic diagram, (b) LNAPL at 11 years, (c) LNAPL at 58 years, (d) DNAPL at 8 years and (e) DNAPL at 41 years.

Example 4. 2-D VE Model Results for Two NAPL Sources

This example concerns NAPL migration from two sources. Two cases involving LNAPL and DNAPL releases are considered. Areal simulations were performed using the VE modeling option. The modeled system is a horizontal aquifer of 3000 meter long, 1000 meter wide and 25 meter thick as shown in Figure 4(a). The top surface of the aquifer is subject to uniform groundwater infiltration of 5 cm/y. The bottom of the aquifer is impermeable. There are two sources that release NAPL at the rate of 1000 kg/y/m² for one year. Ambient groundwater flow is applied as shown in Figure 4(a). The two-dimensional areal domain was discretized using a non-uniform mesh of 378 nodes. Other physical parameters of fluids and the aquifer are the same as those in Table 4.

(a) LNAPL Case

For LNAPL flow simulation, the initial and maximum time step sizes used were 0.1 and 1000 days, respectively. A total of 17 time steps was needed to reach a steady-state condition of the system, at which the final simulation time was 27 years. Figure 4(b) shows the plume of the immobile LNAPL zone when the steady-state was reached.

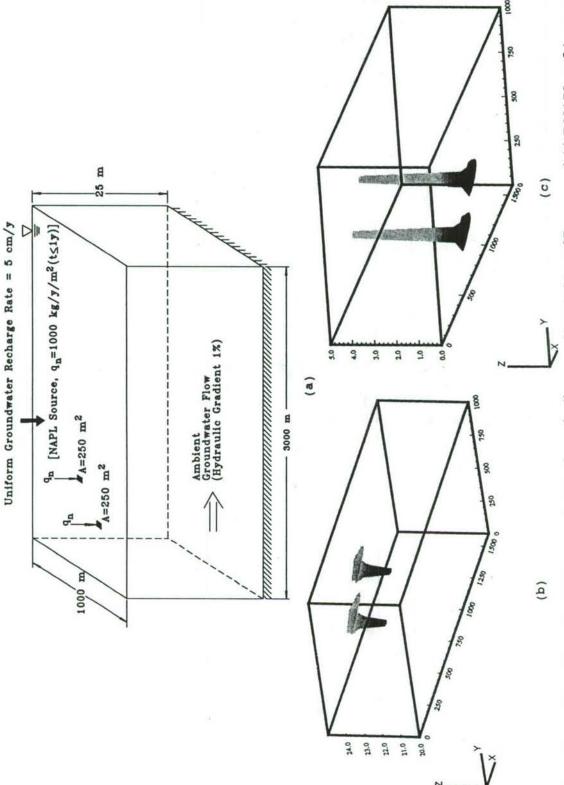
(b) DNAPL Case

For the DNAPL scenario, the same initial and maximum time step sizes were used as for the LNAPL case. The simulation was performed for 15 time steps to reach a steady-state condition at 24 years. The DNAPL pool along the bottom of the aquifer at the steady-state is shown in Figure 4(c).

CONCLUSIONS

A comprehensive two-dimensional model for simulating the subsurface migration of non-aqueous phase liquids (NAPL) has been presented. The model incorporates two approaches based on a rigorous three-phase flow formulation and a gravity-segregated vertical equilibrium formulation. The proposed model overcomes the shortcomings of previous models of NAPL contamination. While the three-dimensional, three-phase modeling approach is the most general one, the requirement on data preparations and computer resources may be demanding. Especially, for large scale, three-dimensional field problems, the demand on the computational resources may be prohibitive. The gravity-segregated sharp-interface VE modeling approach has the advantages of reducing problem dimensions by one and removing complex soil property data requirements. Because of these advantages the VE approach is suitable for preliminary analyses at sites where data availability is limited, large field-scale simulations for which a number of unknowns can reach hundreds of thousands, and sensitivity analyses for which many simulations are required to complete one analysis.

Robust and efficient numerical techniques were implemented to enable practical simulations of site-specific field problems on PC's and workstations. Simulation examples were



Two-dimensional VE example (a) schematic diagram, (b) LNAPL at 27 years and (c) DNAPL at 24 years. Figure 4

Table 4 Physical parameters for the simulation of LNAPL and DNAPL movement in the saturated zone using the VE model

Parameter	Value
Water infiltration	0.05 m/y
Injection rate for LNAPL and DNAPL	$1000 \text{ kg/m}^2.\text{y}$
Injection time for LNAPL and DNAPL	1 y
Aquifer thickness	25 m
Aquifer length	2000 m
Porosity	0.3
Intrinsic permeability	10 ⁻¹² m ²
Water density	1000 kg/m^3
Water viscosity	1.0 cp
LNAPL density	800 kg/m^3
LNAPL viscosity	0.64 cp
DNAPL density	1600 kg/m^3
DNAPL viscosity	1.85 cp

presented to verify the gravity-segregated VE approach and to demonstrate the capability and efficiency of the VE approach. The validation example demonstrated that the VE model can produce results, that are very comparable to the more rigorous three-phase model results, at the fraction of the CPU time required for the multiphase approach.

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FORMULATION OF ALTERNATIVE CHEMICAL PAINT STRIPPERS

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INTRODUCTION

Background

Methylene chloride-based paint strippers have been used extensively by the Army community. Their utility as broad spectrum paint strippers, capable of removing a wide range of coating types, has long been recognized. Methylene chloride use is rapidly being curtailed, however, because of its negative impacts on worker health and the environment. OSHA has proposed a 20-fold decrease in the permissible exposure limits for industrial workers exposed to methylene chloride, an action due in part to its suspected carcinogenicity. Methylene chloride is also listed as an air toxic under amendments to the Clean Air Act.

In 1984 the U.S. Environmental Protection Agency placed a limit of 2.13 mg/l on the allowable concentration of Total Toxic Organics (TTO) which can be discharged from metal finishing operations. U.S. Army installations find it difficult to comply with this regulation when using popular cold chemical paint strippers containing methylene chloride and other TTO chemicals. Many of the strippers in use are also classified as hazardous wastes. Army depots contribute approximately 90% of all hazardous wastes generated by the Army. DoD has mandated a 50% reduction in hazardous waste generation. Proposed legislation could even ban the sale and use of methylene chloride in California.

Previous studies by the Army have focused on evaluating commercially available alternative chemical strippers for dip tank applications. This work has met with limited success. The best materials evaluated require considerably longer contact times for complete stripping. Initial costs of commercial alternatives are relatively high compared to methylene chloride strippers.

Objective

The objective of this study is to formulate alternative chemical paint strippers which are tailored to the specific needs of the Army. Chemical agent resistant coatings and epoxies have proven to be especially difficult to remove with commercially available alternative strippers. More effective strippers are

needed for these coatings. An additional goal is to minimize health and environmental risks and disposal liabilities.

Approach

To test operational success, alternative stripper formulations are first being evaluated in the laboratory. Environmental impact and worker health and safety analyses are being conducted on formulated replacement materials to assure that they are within acceptable levels. Materials meeting the criteria established for performance success in the laboratory and for environmental and worker health and safety will be tested in a small-scale production operation at Sacramento Army Depot (SAAD).

EVALUATION CRITERIA FOR AN ACCEPTABLE PAINT STRIPPER

Criteria for a successful paint stripper were developed in collaboration with SAAD. The following criteria were selected: (1) acceptable stripping speed (SAAD upper limit of 2 hours), (2) effective for a broad spectrum of coatings, (3) not rapidly evaporated or depleted and easily replenished when it does become depleted, (4) no TTO contributing chemicals, (5) environmentally acceptable, (6) safe to use, (7) relatively easy to dispose, (8) compatible with aluminum and steel substrates.

In addition, more specific criteria for environmental, health, and safety evaluation of an alternate paint stripper were selected in cooperation with SAAD. These criteria included factors relating to toxicity (acute and chronic, human and environmental), environmental fate, safety (corrosivity, reactivity, and ignitability), and regulatory restrictions.

SELECTION OF COATINGS AND SOLVENTS FOR TESTING

Using knowledge of coatings chemistry, coatings for stripper testing were selected based on common occurrence in the military inventory and, in some cases, because they represent the hard-to-strip end of the spectrum. Generically, the coatings are zinc-chromate alkyd primer with an alkyd topcoat, water-thinnable epoxy primer with a CARC urethane topcoat, and vinyl-butyral zinc chromate primer with an epoxy polyamide topcoat. Table 1 lists the coatings systems by specification and resin type.

Candidate replacement stripper components were previewed for probable success before inclusion in the test program. Organic strippers may contain any or all the following materials: (1) primary solvents, (2) cosolvents, (3) activators, (4) retarders, and (5) surfactants.

Common solvents in the commercial alternative strippers include 2-(2-butoxyethoxy) ethanol, N-methyl-2-pyrrolidone, monoethanolamine, and aromatic hydrocarbon solvents. Solvents



selected for evaluation in this study are listed in Table 2 and activators in Table 3. A mixture of methylene chloride and formic acid was included in this study as a control against which alternatives will be measured.

Table 1. Coating Systems Selected for Study

Designation Specification for:

	Primer	Topcoat	Coating Type	Substrate Material
A	TT-P1757	TT-E-489	Alkyd/Alkyd	Glass
В	DOD-15328	DOD-15328 MIL-P-2441, Vinyl-butyral/ Formula 152 Epoxy Polyamide		Glass
С	MIL-P-53030	MIL-P-53039	Water Thinned Epoxy/Urethane	Glass

Table 2. Solvents Selected for Study

1.	Methylene chloride (control)
2.	N-methyl-2-pyrrolidone
3.	Tetrahydrothiophene 1-dioxide
4.	2-(2-butoxyethoxy) ethanol
5.	Propylene carbonate
6.	Heptyl acetate
7.	Ethyl 3-ethoxy propionate
8.	Butyrolactone
9.	N-(2-hydroxyethyl)-2-pyrrolidone
10.	Tridecyl acetate

Table 3. Activators Selected for Study

1.	Formic acid
2.	Monoethanolamine

PROCEDURES AND METHODS

Stripper Performance Testing

Each paint system was applied to a uniform thickness on clear plate glass panels measuring 6.0x17.0x0.25 inches. Coatings were applied using a 7-mil Dow draw down blade. Coating thicknesses were measured on representative test panels in accordance with ASTM D4138, Measurement of Dry Film Thickness of Protective Coatings by Destructive Means. Coating adhesion was also determined on representative test panels by ASTM D3359, Tape Test, Method B. Paint removal tests will be conducted after a minimum 30-day ambient air dry period.

Stripping performance will be determined for the neat solvents, neat solvents plus activators, solvent pairs, and solvent pairs plus activators. Performance will be determined as a measure of the time to solvent penetration of the selected coating systems. Time to solvent penetration will be determined with time lapse video equipment. One inch diameter by one inch tall glass cylinders will be used as solvent reservoirs. Time to penetration will be determined for quadruplicate samples of each test material.

A statistical evaluation of the experimental data will be conducted. Performance of each test solution will be analyzed relative to each of the other test solutions. Comparisons will be made between solution performance and solvent properties including solubility parameters, molecular weight, molecular shape, chemical class, pH, boiling point, and dipole moment.

Most users are concerned that acidic paint strippers will cause hydrogen embrittlement of both steel and aluminum substrate materials. This is a valid concern, especially for aircraft maintenance facilities. Basic strippers pose a smaller risk of metal embrittlement. Since users are concerned with the effects of embrittlement we will conduct tests to determine the safety of any stripping material. Many specifications for paint strippers contain embrittlement testing requirements.

Environmental, Health, and Safety Evaluation

To evaluate the environmental, health and safety hazards of the proposed stripper components, we used a procedure to assign numerical ratings to permit quantitative comparison of the hazards associated with each potential stripper component. When specific stripper mixtures are formulated, each mixture will also be evaluated. The rating procedure was developed and used to evaluate commercial alternative paint strippers and their components in a previous study. In this case, the procedure was applied using the criteria selected for this study. Each criterion was scored for every compound. A total score for each component was determined by summing characteristic scores.

The scores for individual characteristics were on scales of 0 to 3 with 0 representing no hazard and 3 representing the greatest hazard. If a score were reported in the literature for a criterion for a chemical, that score was used. In other cases, the same procedure was used to assign a score. If data for assigning a score were lacking, the values were calculated if possible.

RESULTS

The results of hazard ratings of the most promising candidate solvents compared to methylene chloride for environmental, health, and safety hazard criteria are shown in Tables 5 and 6. A higher score indicates a relatively greater risk. These ratings are based on available data from Material Safety Data Sheets and published sources.

Table 5. Solvent Degree of Hazard Scores

CHEMICAL

*	HU MAN	ACUTE ENVIR	The State of the S	BIO ACCUM	PERSIS TENCE	TRANS PORT	CORROS IVITY	REACT IVITY	IGNITA BILITY	TOTAL SCORE
1.	2	1	2	0	3	3	3	1	1	16
2.	2	1	2	NA	1	2	3	0	1	12
3.	2	1	2	0	1	0.5	1	1	1	9.5
4.	2	1	3	0	0	2.5	1	2	2	13.5
5.	1	1	1	NA	1	0	0	1	1	6
6.	1	0	1	NA	1	1	0	1	1	6
7.	1	1	1	0	1	1	0	1	2	8
8.	2	1	3	NA	1	NA	. 0	3	3	13
9.	1	1	NA	NA	NA	NA	0	NA	0	2
10	1	1	NA	0	0	0	0	0	1	3

Table 6. Activator Degree of Hazard Scores

1.	3	1	2	0	0	2.5	3	2	2	15.5
2.	3	1	2	0	0	1.5	3	2	2	14.5

^{*} see Table 2 and Table 3 for chemical names

Compared to methylene chloride, the alternative solvents under evaluation in the laboratory appear to be less hazardous. Also, none of the alternative solvents contribute to TTO discharge. From the hazard scores calculated in this study, however, it is clear that some of the alternative solvents and the activators involve some safety and environmental hazards.

In addition to lower degree of hazard scores, fewer hazardous waste concerns and environmental and health regulations would restrict discharges of the candidate solvents. Compared to methylene chloride, fewer regulatory restrictions overall apply to the candidate solvents, making their use by Army installations more favorable from a standpoint of compliance.

CONCLUSIONS

The established laboratory test protocol has the capacity to yield large amounts of detailed information on the ability of specific solvents and formulated mixtures to remove selected coatings. The experiments are designed to be reasonably reproducible such that additional solvents and formulations may be comparatively evaluated.

Compared to methylene chloride, the alternative solvents evaluated in the laboratory tests appear to be less hazardous. However, it is clear that some of the alternative solvents involve some health, safety and environmental hazards.

We will develop formulations containing the less hazardous components, if they are effective, or use the lowest possible concentrations of the more hazardous components. The technique of the laboratory test protocol designed for this study combined with the hazard assessment permits us to optimize the proportions of selected components to formulate strippers which will maximize performance and minimize the environmental, health, and safety risks.

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